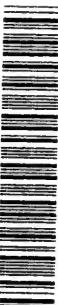


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Researches in spectroscopy
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RESEARCHES IN SPECTROSCOPY AND PERMEABILITY

BY
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*A thesis, submitted in conformity with the requirements for the degree of
Doctor of Philosophy in the University of Toronto*

On the Extreme Ultra-Violet Spectra of the Alkali Metals

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(Communicated by PROF. J. C. McLENNAN, F.R.S.)

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I. Introduction

Some recent work by Professor McLennan¹ on the spectrum of the electrodeless discharge in potassium vapour demonstrated the importance of this type of excitation in the study of the enhanced spectra of the alkali metals. A number of experimenters² have since investigated with this method of stimulation the spectra of sodium, potassium, rubidium, and caesium in the visible and near ultra-violet regions. The object of the present investigation was to extend the study of these enhanced spectra in the extreme ultra-violet by means of a fluorite vacuum spectrograph in order to make additions to the lists of wave-lengths available for series analysis. Of the four metals used potassium alone gave a strong spectrum below the wavelength $\lambda 1850\text{A}$. The spectrum of the discharge in rubidium and caesium vapours was found to include a considerable number of lines between the wave-lengths $\lambda 1850\text{A}$. and $\lambda 2100\text{A}$. that apparently had not been observed by previous experimenters. As the photographs taken with the fluorite spectrograph were not suitable for wave-length measurement above the limit $\lambda 1900\text{A}$. the spectra of rubidium and caesium were also photographed with a small quartz spectrograph. The following paper contains a description of the experiments carried out and the wave-lengths and frequencies of the lines obtained.

II. Description of Apparatus

A diagram of the apparatus and the electrical circuit employed is shown in Fig. 1. The highly evacuated discharge chamber consisted of a Pyrex glass bulb *E* about 8 cm. in diameter with a side tube 32 cm. long. The end of this tube was closed by a window of thin

¹McLennan, Proc. Roy. Soc., v1. 100, 282, 1921.²Zeeman and Dik, Kon. Akad. van Wetensch. te Amsterdam, v1. 25, Nos. 3 and 4, 67, 1922.

Robertson, Phys. Rev., Series 2, v1. 19, 470, 1922.

Dunoyer, Jour. d. Phys. et Rad., Series 6, v1. 3, 261, 1922.

fluorite plate waxed in a brass collar that fitted in the conical opening of the spectrograph tube. The bulb of the discharge chamber was enclosed in an electrical furnace *F* and the temperature was read from the thermometer *T*.

The electrodeless discharge in the vapour was produced by the use of a 10 inch spark induction coil *A*, a spark gap *B*, two sets of Leyden jars *C₁* and *C₂*, and a coil of a few turns of coarse wire wrapped closely about the bulb *E*. These were connected according to the usual type of Tesla discharge arrangement as shown in the diagram. For use as a comparison spectrum and also as a convenient source of radiation for adjusting the spectrograph, the carbon vacuum arc was found very suitable. The arc lamp used consisted of a water-cooled

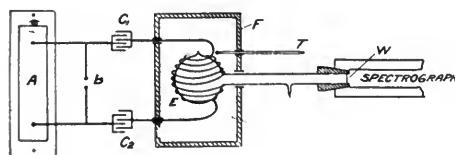


Fig. 1

brass chamber with steel rods as leads entering through oil-sealed joints. Complete details of the lamp have been given in a paper by McLennan and Ainslie,³ by whom it was constructed.

The photographs for the extreme ultra-violet region were taken in a fluorite spectrograph constructed⁴ in this laboratory some time previously. For the work with rubidium and caesium in the quartz region a small Hilger quartz spectrograph specially adjusted for the ultra-violet was used. The photographic plates used with both spectrographs were of the Schumann type and were obtained from the Adam Hilger Co.

III. Experimental

The fluorite spectrograph was adjusted by the use of the carbon vacuum arc as indicated in a previous paragraph until good photographs were obtained with a lower wave-length limit of $\lambda 1323.79\text{A}.$ ⁵ The discharge chamber containing the metal to be investigated was then prepared. The metal was distilled under a high vacuum produced by a mercury diffusion pump through a series of bulbs leading

³McLennan and Ainslie, Proc. Roy. Soc., A, vi. 101, 342, 1922.

⁴McLennan and Lewis, Proc. Roy. Soc., A, vol. 98, 109, 1920.

⁵Shaver, Trans. Roy. Soc. Can., vi. 27, Series III, 131-135, 1923.

to the discharge bulb. The distillation bulbs were then sealed off and after a further thorough evacuation the discharge chamber was sealed off from the pump ready for use. In the case of sodium and potassium lumps of the pure metal were used but with rubidium and caesium the metal was obtained from the chlorides of the metals by the use of powdered calcium metal.

With the discharge chamber mounted in position the temperature of the furnace was raised until the electrodeless discharge produced a bright glow in the bulb. It was found that with the exception of sodium a fainter discharge came on at first, but at higher temperatures a brilliant glow appeared and it was the spectrum of the latter that was photographed. The metal gradually distilled into the side tube which was cooled by the use of wet towels; but by cooling the bulb and warming the tube the process was reversed and the chamber ready for use again.

The induction coil was connected to the 110 volt D.C. mains and was operated on a current of from 8 to 10 amperes with a mercury interrupter. With the fluorite spectrograph the time of exposure was 12 minutes for a photograph of the electrodeless discharge spectrum and about 5 minutes for the comparison spectrum of the carbon vacuum arc. The latter was photographed on the same plate by the use of a shutter that covered a section of the slit. With the quartz spectrograph the electrodeless discharge spectra required an exposure of about 4 minutes as the discharge chamber was placed nearer the slit in this case. The source of the comparison spectrum for the measurement of these plates was produced by a condenser discharge from a $\frac{1}{4}$ kilowatt 10,000 volt transformer between electrodes made of an alloy of aluminium, zinc, cadmium and lead. The spectrum of this spark discharge gave a number of sharp lines well spaced for calculation purposes.

IV. Method of Wave-length Determination

The plates were measured with a Toepler comparator reading to 0.005 mm. The wave-lengths were then calculated by means of a Hartmann dispersion formula $\lambda = \lambda_0 + \frac{c}{n - n_0}$, where λ_0 , c and n_0 were constants determined from the comparison spectrum, and n the distance of the unknown line from a fixed point of reference on the plate. For the fluorite region the standards were obtained from Simeon's measurements of the carbon spectrum.⁶ The wave-lengths

⁶Simeon, Proc. Roy. Soc., A, v1. 102, 484, 1923.

calculated from the plates taken with the quartz spectrograph were based on the measurements of the spectra of aluminium, zinc, cadmium and lead as given in Eder and Valenta's tables.⁷ All wave-length measurements listed in the following tables are on a vacuum basis in terms of the international scale.

On account of the relatively small dispersion of both the fluorite and the quartz spectrographs in addition to the errors of measurement, extreme accuracy cannot be claimed for the results. The dispersion of the fluorite spectrograph above the wave-length $\lambda 1600\text{A}.$ was about 11A. per mm. With the quartz spectrograph the average dispersion between the wave-lengths $\lambda 2300\text{A.}$ and $\lambda 1850\text{A.}$ was 17A. per mm. For all calculation purposes several plates of each spectrum were measured, the wave-lengths determined, and the final results averaged. It is thought that an accuracy of 0.3A. may be claimed for the results with the fluorite spectrograph and 0.2A. for the quartz spectrograph measurements as in the latter case the lines were in slightly better focus which offset the disadvantage of its smaller dispersion.

V. Results

(a) Sodium

The electrodeless discharge first produced luminescence in the sodium vapour at a temperature of about $275^\circ \text{C}.$ It was a brilliant yellow glow apparently filling the whole bulb as Robertson⁸ observed and increased in intensity as the temperature was raised. Several photographs of the discharge spectrum were taken with the fluorite spectrograph when the temperature of the bulb was about $350^\circ \text{C}.$ No lines were obtained in the fluorite region that could be definitely attributed to sodium, the few faint lines present apparently being due to an impurity of carbon monoxide that probably came from the wax used in the discharge chamber.

(b) Potassium

The intense blue discharge in potassium vapour appeared at a temperature of about $250^\circ \text{C}.$ Its spectrum was photographed on the fluorite spectrograph and a number of lines observed that apparently have not been previously recorded. A reproduction of one of the photographs obtained is shown in Plate II (a), and the frequencies and wave-lengths of the lines below $\lambda 1900\text{A.}$ are given in Table I, together with McLennan's results⁹ for the same region.

⁷Eder and Valenta, "Atlas Typischer Spektren," pp. 135-139.

⁸Robertson, *loc. cit.*

⁹McLennan, *loc. cit.* Corrections reducing these wave-lengths to the international vacuum standard were made by the author for the sake of comparison.

Lines that may be due to carbon monoxide or hydrogen impurities have the corresponding wave-lengths as observed by Lyman¹⁰ tabulated adjacent to them.

TABLE 1
POTASSIUM

Int.	ν	λ	Remarks	Int.	ν	λ	Remarks
		I.A. (vac.)	λ I.A. (vac.)			I.A. (vac.)	I.A. (vac.)
2	52751	1895.7	1895.4, McL. ¹¹	6	56472	1770.8	
2	52835	1892.7	1893.1, " 1892.3, "	3	56644	1765.4	
2	52885	1890.9	1891.2, "	0	56689	1764.0	
2	52969	1887.9		0	56893	1757.7	
1	53217	1879.1		1	56944	1756.1	
1	53356	1874.2	1874.5, " 1873.9, "	4	57065	1752.4	
0	53465	1870.4	CO, 1870.3, L. ¹²	8	57166	1749.3	
1	53576	1866.5		4	57432	1741.2	1742.2, McL. ¹¹
1	53709	1861.9		2	57491	1739.4	
1	53859	1856.7		0	57884	1727.6	
0	53920	1854.6		3	57971	1725.0	
2	54233	1843.9		1	58015	1723.7	CO, 1723.9, L. ¹²
2	54342	1840.2		0	58069	1722.1	
2	54434	1837.1	CO, 1837.2, "	3	58085	1721.6	
1	54582	1832.1	Diffuse	3	58146	1719.8	
0	54690	1828.5		3	58500	1709.4	
1	54750	1826.5		3	58675	1704.3	
1	54801	1824.8		9	58703	1703.5	
0	55239	1810.3		10	58862	1698.9	CO, 1698.8, L.
0	55310	1808.0		0	59102	1692.0	
1	55506	1801.6	CO, 1801.9, L. I.A. (vac.)	1	59609	1677.6	
			I.A. (vac.)	2	59698	1675.1	
1	55599	1798.6		3	59776	1672.9	
1	55825	1791.3		{ 4	59905	1669.3	I.A. (vac.)
4	55947	1787.4		{ 4	59927	1668.7	
0	56167	1780.4		4	60252	1659.7	
0	56237	1778.2		1	60383	1656.1	C, 1656.12, S. ¹³
6	56386	1773.5		1	61177	1634.6	
0	56427	1772.2		0?	62348	1603.9	H, 1603.8, L. ¹²
				0	62414	1602.2	Very faint
							H, 1602.0, L.

¹⁰Lyman, "Spectroscopy of the Extreme Ultra-violet," p. 114.

¹¹McLennan, *loc. cit.* Corrections reducing these wave-lengths to the international vacuum standard were made by the author for the sake of comparison.

¹²Lyman, "Spectroscopy of the Extreme Ultra-violet," p. 114.

¹³Simeon, *loc. cit.*

(c) Rubidium

The bright blue violet discharge in rubidium vapour described and investigated by Dunoyer,¹⁴ appeared at a temperature of about 115° C. and was photographed first on the fluorite spectrograph. A very few faint lines were found below the wave-length $\lambda 1850\text{A}.$ but a considerable number of comparatively strong lines appeared between the wave-lengths $\lambda 1850\text{A}.$ and $\lambda 2300\text{A}.$ As the fluorite spectrograph was not suitable for an investigation of this region, photographs were taken on the small quartz spectrograph previously described. Plate II (*b*) shows a reproduction of one of the plates enlarged one and one-half times and Table 2 gives the frequencies and wave-lengths of the lines observed. The impurity in this case was apparently zinc as several lines prominent in the zinc spectrum were present. The wave-lengths in all the following tables quoted from various observers have been corrected to the international vacuum standard where necessary by the author for the sake of comparison.

¹⁴Dunoyer, *loc. cit.*

¹⁵Dunoyer, *loc. cit.* Electrodeless discharge in rubidium vapour.

¹⁶Hagenbach und Schumacher, Zeit. Wiss. Phot., B. 19, 129, 1919. Electrodeless discharge in zinc vapour.

¹⁷Eder und Valenta, Denkschr. Wien. Akad., 68, 531, 1899; "Handbuch d. Spect.", Kayser, B. 6, 854. Zinc spark.

TABLE 2
RUBIDIUM

Int.	ν	λ	Remarks	Int.	ν	λ	Remarks
		I.A. (vac.)	I.A. (vac.)			I.A. (vac.)	I.A. (vac.)
{ 4	43461	2300.9	2300.3, D. ¹⁵	2	46557	2147.9	
{ 4	43484	2299.7		10	46629	2144.6	
3	43558	2295.8		0	46744	2139.3	Zn, 2139.27, E.V. ¹⁷
10	43619	2292.6	2292.8, D	4	46937	2130.5	
1	43653	2290.8	Zn, 2290.6, H.S. ¹⁶	8	47039	2125.9	
3	43704	2288.1		2	47232	2117.2	
1	43927	2276.5		1	47423	2108.7	
0	43958	2274.9		0	47687	2097.0	
6	44076	2268.8		1	47767	2093.5	
0	44138	2265.6	Zn, 2265.69, E.V. ¹⁷	8	47824	2091.0	
10	44156	2264.7		10	48153	2076.7	
0	44193	2262.8		1	48218	2073.9	
10	44344	2255.1	2255.3, D. ¹⁵	6	48319	2069.6	
{ 2	44403	2252.1		0	48426	2065.0	Zn, 2064.92, E.V. ¹⁷
{ 2	44417	2251.4		0	48480	2062.7	Zn, 2062.67, E.V.
1	44448	2249.8		4	48695	2053.6	
1	44500	2247.2		0	48709	2053.0	
1	44573	2243.5	Doublet?	1	48950	2042.9	
4	44671	2238.6		0	49150	2034.6	
3	44907	2226.8		0	49356	2026.1	Zn, 2026.10, E.V.
2	44952	2224.6		0	49778	2008.9	
2	44988	2222.8		0	50213	1991.5	
10	45090	2217.8		1	50327	1987.0	Zn, 1986.9, E.V.
1	45181	2213.3		4	50424	1983.2	
3	45278	2208.6		2	50725	1971.4	
{ 1	45321	2206.5		1	51112	1956.5	
{ 1	45343	2205.4		3	51172	1954.2	
0	45399	2202.7		1	51485	1942.3	Hg, 1942.36, S.K. ¹⁸
10	45479	2198.8	Doublet?	1	51562	1939.4	
3	45639	2191.1		1	52151	1917.5	
2	45813	2182.8		1	52392	1908.7	
2	45864	2181.2		1	52587	1901.6	
0	45869	2180.1		0	52924	1889.5	
0	45907	2178.3		0	52955	1888.4	
1	45950	2176.3					
2	46030	2172.5		1	55233	1810.5	
10	46185	2165.2		0	55435	1803.9	
0	46273	2161.1		0	56789	1760.9	
0	46365	2156.8		0?	58059	1722.4	Very faint
3	46430	2153.8		0	58241	1717.0	

¹⁸Stark und Kinoshita, Ann. d. Phys., B. 21, 470, 1906. Mercury Geissler tube.

(d) Caesium

The investigation of the discharge in caesium vapour was carried out in a manner similar to the experiments with rubidium. The brilliant bluish-white discharge which Dunoyer described as having a many-lined spectrum, appeared at a temperature of about 110° C. Photographs of its spectrum were taken with the fluorite spectrograph and as in the case of rubidium very few lines were found below the wave-length $\lambda 1850\text{A}$. As there was evidence of a large number of lines between this wave-length and the shortest wave-length recorded by Dunoyer,¹⁹ the experiments were repeated with the quartz spectrograph and in Plate II (*c*) is shown a reproduction of one of the photographs enlarged one and one-half times. A list of the frequencies and wave-lengths of the lines observed is given in Table 3, together with those found in this region by Dunoyer in the electrodeless discharge spectrum and by Exner and Haschek²⁰ in the spark spectrum.

It will be noted that the zinc lines present in the rubidium spectrum were not found in the caesium spectrum; and although there are three lines in the latter that agree fairly closely with weak lines in the zinc spectrum, it is thought that this is a coincidence that would not appear with more accurate wave-length determinations. On account of the fact that a mercury diffusion pump was used in the evacuation of both the rubidium and caesium discharge chambers and also that calcium was used in the preparation of the metals, it might be expected that mercury and calcium impurities would be found in both tubes. The only line observed common to the two spectra that might be attributed to either mercury or calcium was the line of wave-length $\lambda 1942.3\text{A}.$, which corresponded to the mercury line $\lambda 1941.77\text{A}$ ($\lambda 1942.36$ I.A. vac.) observed by Stark and Kinoshita.²¹ It is thought therefore that if these impurities were present the amount was practically negligible.

¹⁹Dunoyer, *loc. cit.*

²⁰Exner und Haschek, Leipzig und Wien, 1902; "Handbuch d. spect.", Kayser, B. 5, 389.

²¹Stark und Kinoshita, *loc. cit.* Mercury Geissler tube.

TABLE 3
CAESIUM

Int.	ν	λ	Remarks	Int.	ν	λ	Remarks
		I.A. (vac.)	I.A. (vac.)			I.A. (vac.)	I.A. (vac.)
			2299.2, D. ²²				
8	43509	2298.4		1	45401	2202.6	
4	43643	2291.3	2291.9, D.	6	45426	2201.4	
			2287.7, D.	5	45471	2199.2	
{ 9	43729	2286.8	2286.9, D.	{ 3	45500	2197.8	
			2286.87, E.H. ²³	{ 3	45517	2197.0	
{ 9	43748	2285.8	2285.9, D.	1	45620	2192.0	
			2286.13, E.H.	7	45654	2190.4	
3	43800	2283.1		5	45691	2188.6	
6	43848	2280.6	2278.3, D.	{ 2	45729	2186.8	
10	43966	2274.5	2274.9, D.	4	45811	2182.9	
			2274.54, E.H.	0	45832	2181.9	
10	44086	2268.3	2268.2, D.	9	45867	2180.2	
			2268.32, E.H.	3	45914	2178.0	
			2267.9, D.	4	45947	2176.4	
0	44191	2262.9		0	45975	2175.1	
{ 5	44261	2259.3	2259.0, D.	{ 1	46038	2172.1	
{ 5	44277	2258.5		1	46064	2170.9	
1	44311	2256.8		4	46155	2166.6	
8	44342	2255.2	2255.7, D.	7	46204	2164.3	
8	44516	2246.4	2246.8, D.	{ 2	46286	2160.5	
2	44589	2242.7	Broad	{ 2	46307	2159.5	
5	44659	2239.2		7	46346	2157.7	
2	44739	2235.2	Broad	1	46408	2154.8	
2	44763	2234.0		1	46436	2153.5	
2	44807	2231.8	Broad	1	46484	2151.3	Doublet?
6	44851	2229.6		10	46566	2147.5	Broad
{ 1	44871	2228.6		10	46681	2142.2	Broad
{ 1	44889	2227.7		1	46731	2139.9	
1	44920	2226.2	Broad	2	46779	2137.7	
1	44982	2223.1		2	46806	2136.5	
10	45019	2221.3		1	46834	2135.2	
1	45080	2218.3		10	46896	2132.4	
{ 3	45171	2213.8		8	46984	2128.4	
{ 3	45194	2212.7		0	47021	2126.7	
4	45241	2210.4		1	47223	2117.6	Broad
10	45325	2206.3		7	47288	2114.7	
1	45368	2204.2	Zn, 2204.32, E.V. ²⁴	4	47333	2112.7	

²²Dunoyer, *loc. cit.* Electrodeless discharge in caesium vapour.

²³Exner and Haschek, *loc. cit.*, Caesium spark.

TABLE 3—Cont.
CAESIUM

Int.	ν	λ	Remarks	Int.	ν	λ	Remarks
		I.A. (vac.)	I.A. (vac.)			I.A. (vac.)	I.A. (vac.)
{7	47373	2110.9		1	49329	2027.2	
{7	47398	2109.8		6	49373	2025.4	
1	47506	2105.0	Zn, 2105.12, E.V. ²⁴	3	49414	2023.7	
10	47565	2102.4	Doublet?	6	49468	2021.5	
1	47617	2100.1	Broad	1	49613	2015.6	
1	47644	2098.9		4	49764	2009.5	
1	47694	2096.7		0	49818	2007.3	CO, 2007.2, L. ²⁵
1	47726	2095.3		0	49843	2006.3	
2	47755	2094.0		0	49910	2003.6	
7	47792	2092.4		0	49963	2001.5	
8	47865	2089.2		0	49998	2000.1	
5	47900	2087.7	Zn, 2087.75, E.V.	5	50088	1996.5	
{5	47973	2084.5		1	50203	1991.9	
{5	47994	2083.6		1	50249	1990.1	
8	48063	2080.6		1	50375	1985.1	
{7	48126	2077.9		1	50411	1983.7	
{7	48149	2076.9		1	50467	1981.5	
0	48193	2075.0		1	50587	1976.8	
0	48216	2074.0		1	50646	1974.5	
1	48260	2072.1		0	50720	1971.6	
2	48321	2069.5		0	50810	1968.1	
2	48389	2066.6		0	50847	1966.7	
1	48436	2064.6		0	50961	1962.3	
2	48508	2061.5		2	50984	1961.4	
1	48534	2060.4		1	51143	1955.3	
{6	48565	2059.1		1	51411	1945.1	
{6	48586	2058.2		4	51485	1942.3	Hg, 1942.36, S.K. ²⁶
6	48614	2057.0		0	51515	1941.2	
6	48643	2055.8		2	51578	1938.8	
2	48704	2053.2		1	51616	1937.4	
2	48735	2051.9		0	51653	1936.0	
3	48776	2050.2		8	51674	1935.2	
2	48821	2048.3		1	51789	1930.9	
2	48864	2046.5		0	51948	1925.0	
2	48969	2042.1		2	51991	1923.4	
2	49082	2037.4		1	52083	1920.0	
8	49123	2035.7	Broad	1	52102	1919.3	
6	49247	2030.6		3	52203	1915.6	
{5	49273	2029.5		4	52230	1914.6	
{5	49290	2028.8		0	52351	1910.2	

²⁴Eder und Valenta, *loc. cit.* Zinc spark.

²⁵Lyman, *loc. cit.*

²⁶Stark and Kinoshita, *loc. cit.*

TABLE 3—Cont.

CAESIUM

Int.	ν	λ	Remarks	Int.	ν	λ	Remarks
		I.A. (vac.)	I.A. (vac.)			I.A. (vac.)	I.A. (vac.)
1	52408	1908.1		2	53385	1873.2	
1	52612	1900.7		0	53726	1861.3	
0	52695	1897.7		2	53784	1859.3	
0	52712	1897.1		2	54330	1840.6	
0	52720	1896.8		1	59684	1675.5	
6	52932	1889.2		1	59766	1673.2	
6	53079	1884.0		1	59898	1669.5	
1	53259	1877.6					

VI. Discussion of Results

Although the results with sodium were negative in character it is thought that at a higher temperature, *i.e.*, with an increased vapour pressure, a second spectrum would appear corresponding to the many-lined spectra of the other metals of this group. There was some evidence of an increased brilliance in the discharge with an increase in temperature as Robertson²⁷ also observed, but the apparatus used was not suited to a temperature much higher than 350° C. on account of the rapid distillation of the metal from the bulb into the side tube.

The frequencies of the new lines observed in the spectra of rubidium and caesium have not yet been examined for regularities leading to series relations. In the potassium spectrum the frequencies 53859 and 55599 were found to agree well with the series lines $2p_k - 3.5s''$ and $2p_{III} - 7d$ predicted by Nissen.²⁸ In addition a number of frequencies were noted that agreed within the experimental error with certain combinations of the energy levels calculated by Nissen. A list of the calculated and observed values together with their series notations is given in Table 4.

²⁷Robertson, *loc. cit.*²⁸Nissen. *Astrophys. Jl.*, v1. 57, 185, 1923.

TABLE 4

ν (Calculated)	ν (Observed)	Series notation
53860	53859	$2p_k - 3.5s''$
55600	55599	$2p_{III} - 7d$
Combination Terms		
52895	52885	$2p_k - 4d$
53922	53920	$2p_a - 5d$
54688	54690	$2p_2 - 4.5s'''$
57432	57432	$2p_c - 5d$
58018	58015	$2p_e - 4.5s'''$
58703	58703	$2p_F - 4d$
59112	59102	$2p_g - 4.5s'$
60241	60252	$2p_h - 4.5s'''$

VII. Summary

(1) The spectra of the electrodeless discharge in the vapours of sodium, potassium, rubidium and caesium have been investigated with a fluorite spectrograph.

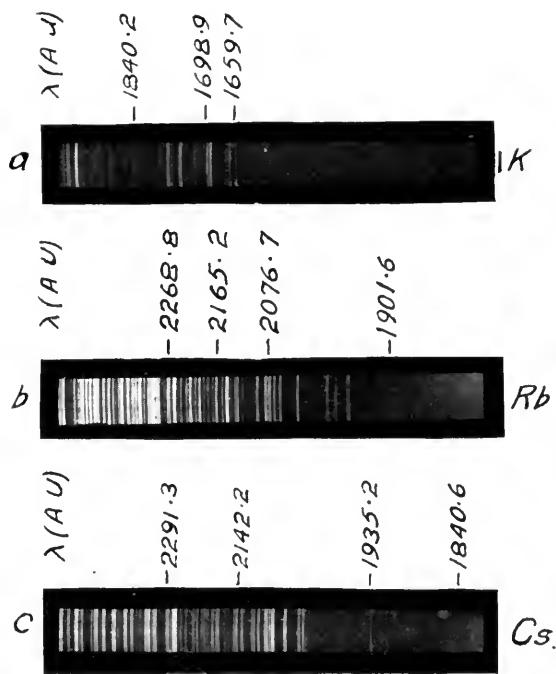
(2) Of the four metals investigated potassium alone gave a strong spectrum in the fluorite region extending to the wave-length $\lambda 1602.2\text{A}$. The frequencies and wave-lengths of the lines were calculated and recorded.

(3) The spectra of the electrodeless discharge in the vapours of rubidium and caesium were also studied in the region between the wave-lengths $\lambda 1850$ and $\lambda 2300\text{A}$. A number of lines in addition to those found by Dunoyer were observed and their frequencies and wave-lengths determined.

(4) A number of frequencies were found in the potassium spectrum that agreed with values predicted from certain energy levels calculated by Nissen for the singly-ionized potassium atom.

In conclusion, the author wishes to thank the members of the Canadian Research Council who made this work possible by the award of a Fellowship, and especially Professor J. C. McLennan, F.R.S., under whose direction this research was accomplished.

The Physical Laboratory,
University of Toronto.
June 30. 1923.



FROM THE TRANSACTIONS OF THE ROYAL SOCIETY OF CANADA

THIRD SERIES—1924

VOLUME XVIII

Note on the Electrodeless Discharge in the Vapours of
Phosphorus and Sulphur

BY

W. W. Shaver, M.A.

OTTAWA

PRINTED FOR THE ROYAL SOCIETY OF CANADA

1924



Note on the Electrodeless Discharge in the Vapours of Phosphorus and Sulphur

By W. W. SHAVER, M.A.

(Presented by PROF. J. C. MCLENNAN, F.R.S.)

(Read May Meeting, 1924)

I. INTRODUCTION

The spectra of phosphorus and sulphur were investigated some years ago in the visible and near ultraviolet regions by a number of experimenters. The most comprehensive work on phosphorus was carried out by Geuter¹ whose measurements on the arc and spark spectrum extended from $\lambda 5727.90\text{A}.$ to a lower wave-length limit of $\lambda 2389.93\text{ A.}$ In the case of sulphur Eder and Valenta² measured the wave-lengths of the lines produced in a Geissler tube discharge in the region from $\lambda 5526.458\text{ A.}$ to $\lambda 3301.211\text{ A.}$ Exner and Haschek³ studied the sulphur spark spectrum and found some eleven lines below this limit, their measurements extending to $\lambda 2856.20\text{ A.}$ The extreme ultraviolet spectra of these two elements was recently investigated by Millikan⁴ who photographed their vacuum spark spectra. His results cover the region between the wave-lengths $\lambda 1646.5\text{ A.}$ and $\lambda 824.5\text{ A.}$ for phosphorus and from $\lambda 1259.3\text{ A.}$ to $\lambda 370.2\text{ A.}$ for sulphur. Hopfield⁵ has also photographed the sulphur arc and spark spectra in the extreme ultraviolet but his published results include only one triplet of wave-lengths above $\lambda 1436.92\text{ A.}$

It will be seen from this summary that there is a lack of information on the spectrum of phosphorus in the region from $\lambda 2400\text{ A.}$ to $\lambda 1650\text{ A.}$ and in the case of sulphur from $\lambda 2850\text{ A.}$ to $\lambda 1430\text{ A.}$ The present experiments were undertaken to investigate at least a part of these unknown regions, with a view to provide wave-lengths for the identification of series due to the singly-ionized, doubly-ionized or multiply-ionized atoms of phosphorus and sulphur. The electrodeless discharge was used as a means of excitation and the

¹Geuter, Diss. Bonn, 1906; Zs. f. wiss. Photogr. 5, p. 1, 1907.

²Eder and Valenta, Denkschr. Wien. Akad., 67, 2, 55 pp., 1898; Beiträge u.s.w., p. 269.

³Exner and Haschek, Leipzig und Wien, F. Deuticke 1911 u. 1912, 3 Bde.

⁴Millikan, Phys. Rev., Vol. 23, p. 1, 1924.

⁵Hopfield, Nature, p. 437, Sept. 22, 1923.

photographs were taken on a vacuum fluorite spectrograph covering the region from $\lambda 1900$ A. to $\lambda 1450$ A. The following paper contains a brief description of the experiments together with tables of the wave-lengths and frequencies of the lines observed.

II. APPARATUS AND EXPERIMENTS

The vacuum fluorite spectrograph, discharge chamber and electrical apparatus employed in the production of the electrodeless discharge were identical with those used by the author in some experiments with the alkali metals. A complete description of this apparatus has been given in an account of that work now in course of publication.⁶ For the experiments with phosphorus a small piece of the yellow variety was inserted in the bulb of the discharge chamber which was then evacuated as thoroughly as possible and sealed off ready for use. In the case of sulphur a small quantity of the yellow powder was placed in the discharge bulb but the side tube of the discharge chamber was left open to the spectrograph so that both the chamber and spectrograph were exhausted simultaneously. The carbon vacuum arc was used as a source of standard lines for wave-length measurements, the carbon spectrum being photographed on the same plate as the unknown spectrum. A movable shutter covering part of the slit enabled one to do this without moving the photographic plate. Schumann plates were used throughout and the time of exposure was about 12 minutes for the spectrum of the electrodeless discharge and 4 minutes continuous arcing for the carbon vacuum arc spectrum.

III. METHOD OF WAVE-LENGTH DETERMINATION

The wave-lengths of the carbon lines used as standard were obtained from Simeon's measurements on the carbon vacuum arc spectrum⁷ and are given in Table I.

TABLE I

λ

I.A. (Vac.)
1930.61
1760.6
1751.8
1657.86

⁶Shaver, "On the Extreme Ultraviolet Spectrum of the Alkali Metals."—Trans. Royal Society of Canada, Section III, 1924.

⁷Simeon, Proc. Roy. Soc., A, Vol. 102, p. 484, 1923.

These values were used to determine the constants λ_0 , c , n_0 in the Hartmann dispersion $\lambda = \lambda_0 + \frac{c}{n - n_0}$, and from the calculated values of these constants and the distances n measured from a fixed point of reference on the plate to the unknown lines, the wave-lengths in the phosphorus and sulphur spectra were determined. The plates were measured with a Toepler comparator reading to 0.005 mm. and the accuracy of the results is thought to be within 0.3 Å. All the wave-lengths and frequencies listed in the tables are based on the International Vacuum scale of measurement.

IV. RESULTS

(a) *Phosphorus*

Under the influence of the electrodeless excitation the phosphorus vapour gave a bright ring discharge at first at room temperature. The electrical discharge, however, caused the rapid disappearance of the yellow phosphorus and a thin red scale was deposited on the inner surface of the discharge bulb. It was then found necessary to heat the bulb to a temperature of about 250° C. before the discharge again appeared. The wave-lengths and frequencies of the lines observed are given in Table II and a reproduction of one of the photographs is shown in Plate XI (a).

TABLE II*

Int.	Frequency	Wavelength	Remarks
		I.A. (vac.)	
3	53781	1859.4	
0	54025	1851.0	
0?	55782	1792.7	Very faint
2	55950	1787.3	
2	56101	1782.5	
2	56348	1774.7	
0	59035	1693.9	
0	59330	1685.5	
1	59545	1679.4	
1	59723	1674.4	
0?	59798	1672.3	Very faint
1	59827	1671.5	

*Since this report was written a paper by Miss M. O. Saltmarsh has appeared in the Philosophical Magazine for May, 1924, on the arc spectrum of phosphorus in the region from 2556.68 Å. to 1671.5 Å. From her work it would appear that nearly all the lines recorded by the present author in the electrodeless discharge spectrum may be attributed to the neutral phosphorus atom. It is worthy of note that the lines of wave-length $\lambda 1674.4$ and $\lambda 1671.5$ that were considered due to an impurity of hydrogen were also observed by Miss Saltmarsh in the arc spectrum and are probably phosphorus lines.

From the reproduction shown and the intensities of the lines listed in Table II it is apparent that the electrodeless discharge spectrum of phosphorus is not very intense in the fluorite region. None of the lines observed, however, were listed by Millikan⁸ in the spectrum of the vacuum spark which apparently gave no phosphorus spectrum in the region studied in the present investigation.

(b) *Sulphur*

The electrodeless discharge in the sulphur vapour produced a bluish white ring luminescence when the temperature was raised to 115° C. Plate XI (b) shows a reproduction of the spectrum obtained and Table III gives the wave-lengths and frequencies of the lines.

TABLE III

Int.	Frequency	Wave-Length	Remarks
		I.A. (vac..)	
0	52532	1903.6	
0?	52607	1900.9	Very faint
6	54705	1828.0	
6	54744	1826.7	op ₁ -1s
6	54879	1822.2	
6	54921	1820.8	op ₂ -1s
6	55276	1809.1	
6	55322	1807.6	op ₃ -1s
2	60006	1666.5	

Three of the strong lines observed are apparently the first triples of the sharp series in the sulphur arc spectrum as worked out by Hopfield⁹ and Birge.¹⁰ Hopfield's measurements of the wave-lengths of these lines are respectively $\lambda 1826.35$, $\lambda 1820.53$ and $\lambda 1807.42$. In the spectrum of the electrodeless discharge there appeared a second line near each member of this triplet as will be noted from the table.

V. SUMMARY

(1) The spectrum of the electrodeless discharge in phosphorus vapour was studied in the fluorite region and the lines observed were measured and tabulated.

(2) The spectrum of the electrodeless discharge in sulphur vapour was also investigated and the wave-lengths and frequencies of the lines were recorded. The first triplet of the sharp series in the sulphur arc spectrum came out with good intensity.

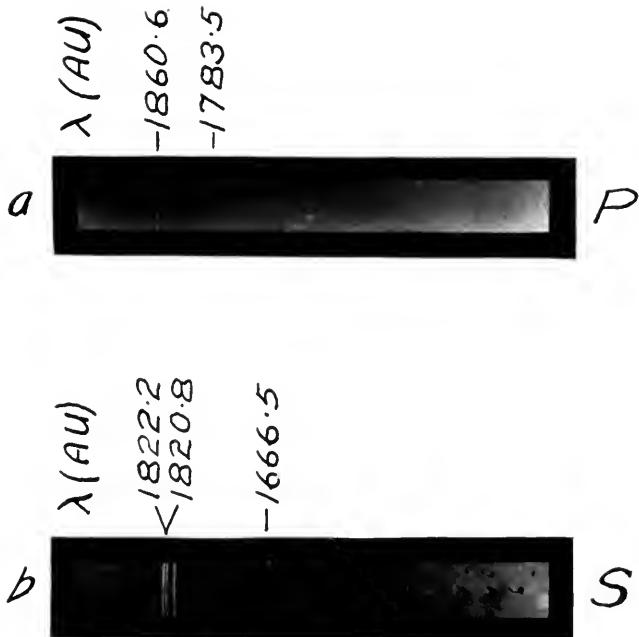
⁸Millikan, *loc. cit.*

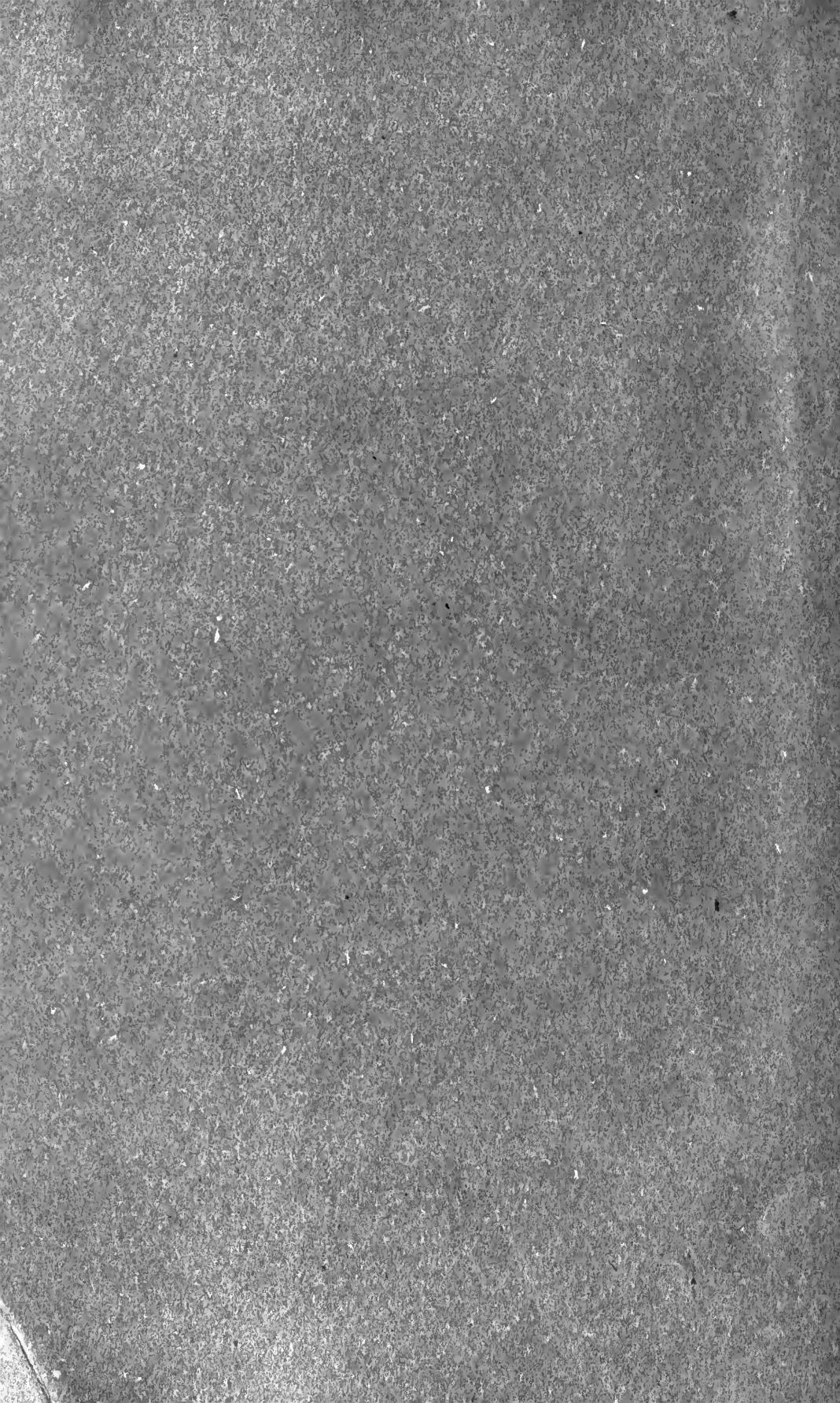
⁹Hopfield, *loc. cit.*

¹⁰Birge, *Jl. Opt. Soc. Am.*, Vol. 8, p. 233, 1924.

In conclusion the author wishes to express his sincere gratitude to the members of the Canadian Research Council who made it possible for this work to be done, and in particular to Prof. J. C. McLennan who suggested the problem and under whose direction the work was carried out.

The Physical Laboratory,
University of Toronto,
May 1, 1924.





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THIRD SERIES—1923

VOLUME XVII

Note on the Extreme Ultraviolet Spectrum of the Carbon Arc

By

W. W. Shaver, M.A.

OTTAWA

PRINTED FOR THE ROYAL SOCIETY OF CANADA

1923



Note on the Extreme Ultraviolet Spectrum of the Carbon Arc

By W. W. SHAVER, M.A.

(Presented by PROFESSOR J. C. McLENNAN, F.R.S.)

(Read May Meeting, 1923)

I. Introduction

The ultraviolet spectrum of carbon has been the subject of many investigations during the past few years, the most recent having been carried out by Simeon,¹ who photographed the spectrum of the carbon vacuum arc between the limits 2512.44 and 595.1 Å. The author had occasion to adjust the lenses and prism of a fluorite spectrograph, and finding the carbon vacuum arc to be very suitable for testing purposes, took several photographs of its spectrum in the Schumann region. On examination of the spectrograms and comparison with the work of Simeon it was found that the shortest wavelength obtained was 1329.79 Å., the spectrum showing up in very good detail. All the lines recorded by Simeon between 1930.61 Å. and the above mentioned lower limit were present on the plate. In addition several other lines appeared, some of which have been recorded by Millikan² and Wolff³, and seven others that are apparently new. The following gives an account of the experiments and the wavelengths of the lines obtained.

II. Apparatus

The fluorite spectrograph used has been fully described in a paper by McLennan and Lewis,⁴ to which the reader is referred. The only change made in the instrument was the substitution of new fluorite lenses and prism obtained from the Adam Hilger Company, as the others had deteriorated, becoming extremely flaked showing cleavage planes.

The vacuum arc lamp used has also been described in a paper by McLennan and Ainslie.⁵ It consisted of a water-cooled brass

¹Simeon, Proc. Roy. Soc., A., vol. 102, pp. 484-496, 1923.

²Millikan, Astrophys. Jl., vol. 52, pp. 47-64, 1920; Astrophys. Jl., vol. 53, pp. 150-160, 1921.

³Wolff, Ann. der Phys., vol. 4, 42, pp. 825-839, 1913.

⁴McLennan and Lewis, Proc. Roy. Soc., A., vol. 98, 1920, pp. 109-114.

⁵McLennan and Ainslie, Proc. Roy. Soc., A., vol. 101, July 1, 1922, pp. 342-348.

chamber having two insulated electrodes inclined at an angle of 90° entering by two side tubes, with oil seals to render the junctions vacuum tight. Solid carbon rods 3/8" in diameter were clipped to the electrodes of the lamp which were connected through a suitable resistance to the 110 volt D.C. mains.

III. *Experiments*

The lamp was mounted in position joined to the spectrograph by a side tube at right angles to the plane of the electrodes with a carefully ground joint that fitted in the conical opening at the end of the spectrograph tube carrying the collimating lens and slit. The joint was made vacuum tight by means of soft wax and the whole apparatus exhausted by means of two Trimount oil pumps in series. The vacuum was tested by means of a Geissler tube operated by a small 4-volt induction coil. Hydrogen was used for washing out the system and evacuation carried on until a green fluorescence showed in the Geissler tube. The arc was then started by manipulating the electrodes until the carbons touched, and at the end of a few seconds' arcing, the circuit was broken until the gas that had been liberated from the hot carbons had been removed by the pumps. The current used in operating the arc was about 8 amperes and the time of exposure was equivalent to about 5 minutes' continuous arcing. The photographic plates were of the Schumann type and were obtained from the Adam Hilger Company.

The prism and lenses of the instrument had been previously adjusted for the line of wavelength 1854 Å. in the aluminium spark spectrum and then using the carbon arc as a source of radiation further adjustments were made until good photographs were obtained with a lower wavelength limit of 1323.79 Å. Several photographs of the spectrum of the carbon vacuum arc were then taken from which the measurements were made.

IV. *Method of Determining Wavelengths*

The plates were measured with a Toepler comparator reading to one two-hundredth of a millimetre. Several prominent lines were identified with those obtained by Simeon⁶ (marked with an asterisk in Table 1), and his measurements of the wavelengths were used as standards. The wavelengths of the other lines in the spectrum were then calculated by means of a Hartmann dispersion formula, and as the standard wavelengths were vacuum values, the calculated measurements are on the vacuum basis as well.

⁶*Loc. cit.*

A number of plates were measured and the average taken of the wavelengths obtained. However, on account of (1) the errors in determining the centre of the line; (2) the small dispersion (14.3 Å. per mm.) at the longer wavelength end of the spectrum; and (3) the scarcity of standard lines between 1930.61 and 1657.86 Å., an accuracy greater than 0.3 Å. cannot be claimed for the region of the longer wavelengths. At the extreme ultraviolet end the dispersion was 3.3 Å. per mm. and it is thought reasonable to presume an accuracy of 0.2 Å. in this section of the spectrum.

V. Results

A comparison of the lines obtained by Millikan⁷ in the hot-spark spectrum of carbon, by Simeon⁸ in the vacuum arc and by the author in the present investigation is given in Table 1. Plate I shows a reproduction of one of the photographs obtained. It will be noted that all the lines obtained by Simeon were observed by the author as mentioned in a previous paragraph. In addition lines of wavelength 1826.3, 1623.8, 1362.2 Å. respectively were recorded corresponding apparently to the lines 1827.3, 1624.3 and 1362.6 that Millikan found in the hot-spark spectrum, the latter two of which he attributes possibly to boron and calcium respectively. The line of wavelength 1826.3 Å. had previously been recorded by Wolff, using a carbon vacuum arc with a fluorite spectrograph as had also the line $\lambda = 1820.5$ Å. By the use of a very narrow slit the four components of the line at $\lambda = 1657$ Å. were brought out as observed by Simeon, the two central ones being very close together. Of the seven new lines two may be due to impurities, but it is thought that the other five must belong to the carbon spectrum. The carbon electrodes were taken from ordinary commercial arc carbon, and although no test was made as to their chemical composition, the absence of metallic lines would indicate that the percentage of impurity present was very small. This is the more likely as Simeon obtained the same spectrum with pure carbon as with commercial carbon with the exception of the mercury line at $\lambda = 2536$ Å., which he attributed to an accidental contamination with some mercury.

The fact that the doublet at $\lambda = 1335.66$ and $\lambda = 1334.44$ Å. came out with such great intensity shows that it must be particularly strong in the carbon arc spectrum as it appears at about the limit of the transparency of the fluorite spectrograph. It is interesting to note also that in the region studied Millikan found only two lines in the hot-

⁷Loc. cit.

⁸Loc. cit.

TABLE I

Int.	1 Millikan. Hot spark spectrum. Grating spectrograph	Int.	2 Simeon. Vacuum arc spectrum. Grating spectrograph	Int.	3 Author. Vacuum arc spectrum. Fluorite spectrograph	4
7	1931.1	5	1930.61*	8	1930.61	
0	1910.2			2	1826.3	1826.30, Wolff ⁹
1	1827.3			1	1820.5	1820.47, Wolff
				1	1816.9	
			1	1807.7	0	1807.5
			2	1760.6*	4	1760.6
2	1752.3	2	1751.8	4	1751.9	
				2	1721.5	
5	1657.6	8	1657.86*	10	1657.86	
		8	1657.20	10	1657.1	
		8	1656.81	10	1656.8	
		8	1656.12*	10	1656.12	
1B?	1624.3			3	1623.8	
				0	1602.8	1603.3 CO, Lyman ¹⁰
1	1577.6					
5	1561.3	9	1561.32*	10	1561.32	
		9	1560.67	10	1560.6	
		9	1560.16*	10	1560.16	
3	1550.9	2	1550.8	2	1550.8	
4	1548.4	3	1548.3	3	1548.2	
1	1482.1	3	1481.7*	3	1481.7	
				0	1470.1	
				0?	1468.3	Very faint
		2	1467.4	2	1467.4	
				0?	1465.8	Very faint
2	1463.7	4	1463.3*	6	1463.3	
		2	1459.1	2	1459.0	
1	1432.2	2	1431.6*	4	1431.6	
1	1426.9					
4 Si?	1402.9					
Ca?						
4 Si?	1393.9			1	1378.6	{ 1378.1 CO, Lyman
Ca?						{ 1378.1 N, Hopfield ¹¹
5 Ca?	1362.6			1	1362.2	
1	1356.2	1	1355.7	0	1355.8	
15	1335.0	10	1335.66*	10	1335.66	
		10	1334.44	10	1334.4	
		8	1329.60	4	1329.6	
		8	1329.07*	4	1329.07	
1	1323.7	7	1323.79*	2	1323.79	

spark spectrum of intensity greater than unity which did not appear in the arc spectrum photographed by the author; and in a recent paper Fowler¹² has shown that both of these lines belong to silicon.

Summary

1. The carbon arc spectrum has been photographed on a fluorite spectrograph between the limits 1930.61 and 1323.79 Å.

2. All the lines found by Simeon were recorded and in addition ten others, three of which correspond to lines found by Millikan in the hot-spark spectrum.

3. The lines at 1624.3 and 1362.6 Å. which Millikan possibly attributed to boron and calcium respectively were recorded in the arc spectrum and apparently belong to carbon.

In conclusion, the author wishes to express his gratitude to the Canadian Advisory Council for Scientific and Industrial Research, who made it possible for this work to be done. He also wishes to express his indebtedness to Professor J. C. McLennan, F.R.S., under whose direction the research was carried out and to both Professor McLennan and Mr. D. S. Ainslie, who had previously constructed the arc lamp used throughout the work.

The Physical Laboratory,
University of Toronto,
June 15, 1923.

⁹*Loc. cit.*

¹⁰Lyman, "Spectroscopy of the Extreme Ultraviolet," p. 114.

¹¹Hopfield, Phys. Rev., Dec., 1922, pp. 573-588.

¹²Fowler, Proc. Roy. Soc., A., vol. 103, p. 413, June 1, 1923.

λ (A.U)

-1930.61

-1760.6

-1657.86

-1561.32

-1463.3

-1378.6

-1362.2

-1323.79



CARBON VACUUM ARC SPECTRUM
PLATE I



FROM THE TRANSACTIONS OF THE ROYAL SOCIETY OF CANADA

THIRD SERIES—1922

VOLUME XVI

Arc, Spark and Absorption Spectra of Argon

BY

W. W. Shaver, M.A.

OTTAWA

PRINTED FOR THE ROYAL SOCIETY OF CANADA

1922

Arc, Spark and Absorption Spectra of Argon

By W. W. SHAVER, M.A.

Presented by PROFESSOR J. C. MCLENNAN, F.R.S.

(Read May Meeting, 1922)

A. *On the Arc and Spark Spectra of Argon*I. *Introduction*

The resonance and ionization potentials of argon have been accurately determined by Rentschler,¹ Horton and Davies,² Déjardin³ and others. The spectrum of the radiation produced by the bombardment of argon atoms with electrons of various speeds has also been studied by Déjardin,⁴ using the well-known lamp of the three-electrode type with accelerating potentials varying from 16 to 80 volts. He found that with potentials from 16 to 33 volts the lines in the spectrum of the radiation produced all belonged to the red spectrum of argon. The blue spectrum which is due to the excitation of the ionized argon atoms began to appear with a field of 34 volts and the number of lines increased with increasing accelerating potential.

The author has repeated these experiments using potentials varying from 10.1 to 240 volts. The results obtained for the most part substantiate the work of Déjardin with this one exception. It was found that a visible radiation persisted with a voltage of 10.1 volts after the arc had once been struck, whereas Déjardin found that the lowest possible voltage required to excite radiation was between 15 and 16 volts and then it was only detected with an exposure of three hours. The production of this radiation with a grid potential of 10.1 volts, which is approximately the resonance potential of argon, required very exacting experimental conditions as to the gas pressure and the proximity of the filament to the grid, but it was found possible to photograph it with an exposure of half an hour. The spectrum obtained consisted of lines belonging to the red spectrum of argon and some bands, which were probably due to traces of gas impurities from the wax used with the quartz window.

¹Rentschler, Phys. Rev., Vol. 14, p. 503, Dec., 1919.

²Horton and Davies, Roy. Soc. Proc. A, Vol. 97, p. 1, March 1, 1920.

³Déjardin, Comptes Rendus, Vol. 172, 1921, p. 1347.

⁴Déjardin, Comptes Rendus, Vol. 172, 1921, p. 1482.

Professor J. J. Thomson⁵ has shown by positive ray analysis that the argon atom may lose several electrons, and it was hoped that by use of a high accelerating potential a third spectrum due to a highly ionized type of atom might appear. However, with a voltage of 240 volts between the filament and the grid no new lines were brought out.

II. Description of Apparatus

As there was no effort made to determine the resonance or ionization potential a simple lamp of the three-electrode type was used (see Fig. 1). The lamp made of Pyrex glass was cylindrical in shape, 15 cm. long and 3.5 cm. in diameter. Two electrodes of coarse tungsten wire were sealed in at one end and a 9 mil tungsten filament F was silver soldered to these electrodes. The other end of the lamp was closed by a quartz window securely sealed with wax. The grid G consisted of two concentric cylinders of fine iron wire gauze, having a mesh of 12 wires to the inch, the inner one being supported by the outer by means of short lengths of iron wire which were silver soldered to both. The inner gauze cylinder was about 1.5 cm. in diameter and the one end was closed by a circular iron plate S . Thus when the grid was in position the plate S prevented the light produced by the heated filament from reaching the slit of the spectrograph. The third electrode, which was also of tungsten wire, was sealed in the side of the lamp and silver soldered to the grid.

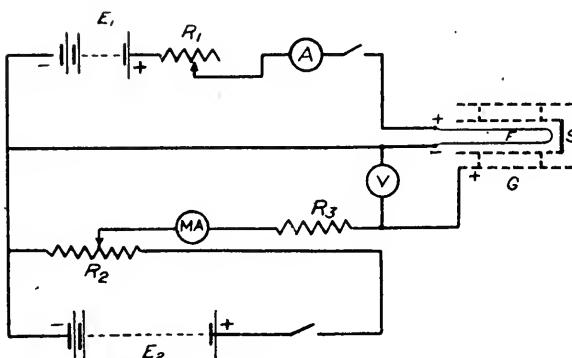


Fig. 1

All metal parts were first heated to red heat and then cleaned with acid. The lamp was then mounted in an electric furnace in such a way that the quartz window dipped in a water bath which

⁵Thomson, *Rays of Positive Electricity*, First Edition, p. 53.

prevented the wax from melting. Exhaustion was carried on for about twenty hours by means of a mercury pump and also a charcoal tube immersed in liquid air, the temperature of the furnace being maintained at 400°C. The filament was also heated to incandescence by passing a current through it while the lamp was being exhausted so that any gas which might be given off was removed. The argon gas was purified from a mixture of 80 per cent. argon and 20 per cent. nitrogen by repeatedly passing it over calcium turnings heated to 600°C., and after the pump and the charcoal tube were sealed off, some of this purified gas was admitted to the tube. The best gas pressure for the production of the arc was found by trial to be about 0.1 mm. of mercury, after which the lamp was sealed off and ready for use.

The electrical connections are also shown in Fig. 1. The current for the heating circuit was supplied by a 20 volt battery E_1 , which was connected in series with a variable resistance R_1 , an ammeter A , and the filament F . The grid voltage was obtained from a second battery E_2 , which was short-circuited through a resistance R_2 of about 115 ohms. Any voltage not exceeding 240 volts, the maximum of the battery, could be applied between the filament and the grid.

III. *Experiments*

The heating current required to bring the tungsten filament to the temperature necessary for the emission of electrons was at first 5.8 amperes, but as the filament gradually evaporated and thus decreased in diameter this amperage was reduced by increasing the resistance R_1 so as to keep the electron supply constant. The electrons were given a definite speed depending on the grid voltage while traversing the distance between the filament F and the inner cylinder of the grid. Any electrons which passed through the meshes of the inner cylinder then entered the fieldless space between the cylinders, since the latter were connected by iron wire as previously described. When the grid voltage was sufficient to give the electrons the energy required to cause inelastic impact with the argon atoms, radiation was produced in the space between the cylinders. This was focussed on the slit of a large quartz spectrograph made by the Adam Hilger Company and photographed on Wratten panchromatic plates. It was found that with an exposure of half an hour good photographs were obtained. The current passing from the filament to the grid was kept as near to 35 milliamperes as possible, except in the case where the grid voltage was 10.1 volts when it fell to 10 milliamperes.

IV. Results

Photographs were taken with the following accelerating potentials: 10.1, 16, 19, 30, 31, 37, 40, 45, 55, 90, 105 and 240 volts. At 10.1 volts, which was the minimum voltage for radiation, the following lines belonging to the argon red spectrum appeared:

Intensity	Wave-lengths in Å.U.
0	4335.4
0	4300.2
1	4259.8
2	4198.4
2	4158.7
1	4055.9

A reproduction of the photograph taken is shown in Plate I(*a*). The faint lines are the ones whose wave-lengths have been given while the bands occurring at the wave-lengths 3806.4, 3562.0 and 3347.9 Å.U., which are plainly seen in the photograph, are probably due to traces of gas impurities from the wax used with the quartz window. These bands did not appear in the other photographs taken with higher accelerating potentials, which was doubtless due to the much greater relative intensity of the argon arc. The fact that this radiation appeared with an accelerating potential of 10.1 volts, whereas the resonance potential has been found to be 11.5 volts,⁶ is due to the initial energy of the electrons as they came out from the heated filament, for which no correction was made.

Plate I(*b*) shows a reproduction of the spectrum obtained with a grid voltage of 16 volts, which is approximately the ionization potential of argon. At this voltage a large number of lines, all belonging to the red argon spectrum appeared, the intensities of the various lines, of course, being somewhat different from the red spectrum produced by passing an induction coil discharge through an argon discharge tube, a reproduction of which is shown in Plate I(*c*). This agrees with the results of Déjardin and indicates that the red argon spectrum is due to the return of a single electron which has been removed by the bombarding electron moving with a speed corresponding to a fall in potential of 16 volts, or in other words, the red argon spectrum is produced by a recombination of a singly ionized argon atom with an electron. The photograph in Plate I(*d*) shows the mercury arc spectrum for wave-length comparison.

⁶Horton and Davies, loc. cit.

In Plate II are shown reproductions of photographs taken with accelerating voltages varying from 31 to 105 volts. Up to 30 volts potential on the grid only lines belonging to the red argon spectrum appeared. However at 31 volts some faint lines belonging to the blue or enhanced spectrum became evident (see Plate II(*a*)). As the voltage was increased these lines became more intense and others appeared as shown in Plate II(*b*), which was taken with a grid potential of 37 volts. Plate II(*c*) shows the spectrum of the arc when the accelerating potential was 40 volts, in which the number and intensities of the lines belonging to the blue spectrum were still further increased. These results do not exactly agree with those of Déjardin, who found that the lines of the enhanced spectrum did not appear until an accelerating potential of 34 volts was used. This discrepancy may be accounted for by the fact that in the present experiments the temperature of the filament may have been slightly greater than that used by Déjardin, which would mean that the bombarding electrons had a greater initial velocity and therefore required a smaller accelerating field to give them the same energy.

Plate II(*d*) shows the result with a grid potential of 54 volts. It is to be noted that, according to the Bohr theory, the potential necessary to give an impacting electron the required energy to remove both electrons from the helium atom is 54 volts. Hence the energy required to remove two electrons from any other neutral atom of higher atomic number than helium, is less than that corresponding to 54 volts owing to the repulsive force exerted by the remaining electrons. Thus with a grid potential of 54 volts all the lines of the enhanced spectrum of argon should be present. This would appear to be the case, as apart from changes in intensities, the spectrum was unchanged when a potential of 105 volts was used (see Plate II(*e*)). Some of the lines in the ultra-violet between the wave-lengths 2900 Å.U. and 2300 Å.U. are very faint and do not appear in the reproduction so that the agreement between the arc spectrum at 54 volts and the blue spark spectrum shown in Plate II(*f*) was much better than the reproductions would indicate. The spectrum in Plate II(*g*) is that of the mercury arc which, as before, was used for wave-length comparison purposes. It will be noted that the mercury line of wave-length 2536 Å.U. appears on several of the photographs, which was due to a trace of mercury vapour in the lamp.

V. Conclusions

The conclusions to be drawn from these results are necessarily somewhat indefinite. It seems clear, however, that with a speed

corresponding to a fall in potential of about 31 volts a bombarding electron has sufficient energy to ionize the argon atom and to disturb a second electron to a certain degree. As the voltage is further increased the second electron is removed to a greater distance from the nucleus, but it is difficult to say at what voltage the atom is doubly ionized by the complete removal of two electrons.

There is also the possibility of removing more than two electrons from the atom and it was thought that a new type of spectrum might be brought out by increasing the accelerating potential. A photograph was taken with a grid voltage of 240 volts, but the results were negative as no new lines were brought out.

VI. *Summary*

1. The radiation produced in argon by electron bombardment with an accelerating potential of 10.1 volts has been detected photographically, and a table of wave-lengths is given.
2. With accelerating fields varying from 16 to 30 volts the lines in the arc spectrum were found to belong to the red argon spark spectrum.
3. As the grid potential was further increased to 31 volts the blue or enhanced spectrum began to appear. At 54 volts apparently all the lines in the enhanced spectrum were in evidence as predicted by the Bohr theory.
4. An attempt was made to bring on a third type of spectrum by use of a grid potential of 240 volts. The results of this experiment were negative as no new lines appeared.

B. *On the Absorption Spectrum of Argon*

I. *Introduction*

In a recent paper on the ionized spectrum of potassium, Professor McLennan⁷ has shown that a moderate electrodeless discharge in potassium vapour produces a spectrum presumably due to the singly ionized atoms, which exhibits a striking similarity to the arc or red spectrum of argon. He has also shown that when potassium vapour is excited by a violent electrodeless discharge a new spectrum appears which resembles to a marked degree the enhanced or blue spectrum of argon. These experiments strongly support the theory suggested by Sommerfeld,⁸ that the enhanced spectrum due to the singly ionized

⁷McLennan, Proc. Roy. Soc. A, Vol. 100, p. 182, 1921.

⁸Sommerfeld, Atombau und Spektrallinien, p. 296.

atoms of any element should resemble the ordinary or arc spectrum of the element immediately preceding it in the table of the elements. If the ionization of the atoms is such as to remove two electrons, according to this theory the spectrum due to the remaining system should resemble the enhanced spectrum of the immediately preceding element. This is a consequence of the theory that the outer electronic configuration of the ionized atom of any element whose atomic number is N , is the same as that of the neutral atom whose atomic number is $(N-1)$; and similarly that the arrangement of the outer electrons in the doubly ionized atom of atomic number N , is identical with that of the singly ionized atom of atomic number $(N-1)$, and also the neutral atom whose atomic number is $(N-2)$. This is readily seen from the diagrams of atomic models shown in Fig. 2.

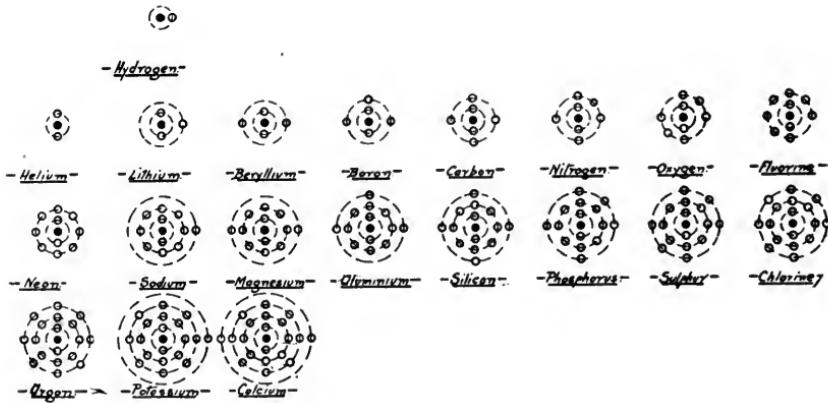


Fig. 2

The purpose of this investigation was to make a further test of Sommerfeld's prediction by comparing the absorption spectrum of argon in various states of ionization with that due to neutral and ionized atomic chlorine or sulphur, since chlorine and sulphur are the elements immediately preceding argon in the table of the elements. Accordingly a study has been made of the absorption spectrum of argon both neutral and ionized by various means, between the wavelengths $\lambda = 7000 \text{ \AA.U.}$ and $\lambda = 2150 \text{ \AA.U.}$ In no case was a definite absorption observed either with the ionized gas or with the ordinary gas at a pressure of 102.4 atmospheres. Up to the present time the author has not investigated the absorption spectra of atomic chlorine and sulphur so that in this paper the experiments with argon alone are described. However, from the negative results obtained with ionized argon, it may be predicted on the basis of the Sommerfeld

theory that neutral atomic chlorine should have a similarly transparent region, shifted slightly towards the infra-red on account of the smaller mass of the chlorine nucleus. Molecular chlorine has some well-known absorption bands in the visible region and it would be very interesting to see if these bands could be made to disappear by the disruption of the chlorine molecules into atoms. Further research is needed to determine this point.

II. *Experiments with Ionized Argon*

(a) The absorption tube consisted of a quartz tube 40.3 cm. long and 1.5 cm. in diameter, having clear quartz windows fused in at each end and two side tubes in which discharge terminals were sealed. The argon used was obtained as before by repeatedly passing a mixture of 80 per cent. argon and 20 per cent. nitrogen over turnings of calcium metal maintained at a temperature of 600°C. The absorption tube was thoroughly exhausted and then filled with purified argon gas at a pressure of 2 mm. of mercury. The light from the electric spark between aluminium terminals under distilled water⁹ was focussed on the slit of the large quartz spectrograph used in the previous experiment and the absorption tube was placed in the path of the light between the focussing lens and the spectrograph slit. The gas in the absorption tube was feebly ionized by passing a weak discharge from a four volt induction coil between the discharge terminals in the side tubes. With the absorbing column of gas in this ionized condition the light from the discharge between the aluminium terminals under water was passed through the tube into the spectrograph and allowed to fall upon a Wratten panchromatic plate for one and three-quarters hours. The aluminium spark under water gave a beautifully continuous spectrum between the wave-lengths $\lambda = 7000 \text{ \AA.U.}$ and $\lambda = 2150 \text{ \AA.U.}$, but there was no evidence of any absorption whatever due to the ionized argon.

The experiment was repeated using as a source of radiation the blue argon discharge produced by passing the discharge from a condenser through an argon Geissler tube made of quartz. If the blue spectrum is due to a disturbance of electrons in the singly ionized atom, then argon gas, when feebly ionized, should be in a condition to absorb this blue radiation. The gas in the absorption tube was excited as before by a very weak discharge, so that it was in a feebly ionized condition. The time of exposure was one hour and forty minutes, but there was no indication of any absorption of the blue radiation.

⁹Henri, Phys. Zeit., No. 12, p. 516, June 15, 1913.

(b) The absorption tube was then re-exhausted and filled with pure argon at a pressure of 155 mm. of mercury. To produce ionization in the gas at this pressure necessitated a stronger discharge, so that in this experiment the discharge terminals in the absorption tube were connected in series with the argon discharge tube, which was again used as a source of radiation. A heavy condenser discharge was passed through the circuit, ionizing the gas in the absorption tube and at the same time giving the blue argon discharge in the Geissler tube. The light from the latter was passed through the absorption tube and brought to a focus on the slit of the spectrograph. The exposure in this case was twenty-five minutes but, as before, no definite absorption was observed.

This experiment was repeated, using a Tesla coil of heavy wire wound about the absorption tube to produce ionization of the gas. This coil was connected in series with the discharge tube and a strong Tesla discharge passed through the circuit. No absorption of the blue spectrum was detected with an exposure of thirty minutes.

(c) The tube was refilled with argon at a pressure of 5 mm. of mercury. Several experiments were performed similar to those previously described in an attempt to produce an absorption spectrum, but the results were again negative.

(d) A quartz bulb 6 cm. in diameter was filled with argon gas at a pressure which gave a brilliant glow when the bulb was placed in a coil through which a Tesla discharge was passing. The bulb was placed in the Tesla coil and mounted in front of the slit of the spectrograph. The coil was connected in series with the terminals of the quartz Geissler tube filled with argon and a Tesla discharge from a twenty volt induction coil passed through the circuit. The light from the blue discharge in the Geissler tube was passed through the quartz bulb and focused on the spectrograph slit. The time of exposure was sixteen minutes, but there was no indication of any absorption of the blue argon spectrum by the ionized gas in the bulb.

III. Experiments with Argon at High Pressure

The author has already investigated the absorption spectra of oxygen and nitrogen between the wave-lengths $\lambda = 7000 \text{ \AA.U.}$ and $\lambda = 2150 \text{ \AA.U.}$, and it was thought that it might prove interesting to examine the absorption spectrum of argon in this region. The absorption tube used and the arrangement of apparatus was precisely as in the experiments with oxygen and nitrogen, which have already been described in a previous paper.¹⁰ The absorption chamber was

¹⁰Shaver, Trans. Roy. Soc. Can., p. 7, 1921.

a brass tube 35 cm. long and 1.5 cm. in diameter, having quartz windows 1.2 cm. in thickness securely held by brass caps screwed to the tube. The source of radiation was the spark between aluminium terminals under distilled water, which gave a continuous spectrum between the wave-lengths previously mentioned. The light from this spark was passed through the absorption tube filled with the gas and brought to a focus on the spectrograph slit.

The gas in the absorption chamber consisted of a mixture of 80 per cent. argon and 20 per cent. nitrogen at a pressure of 128 atmospheres and was obtained from the Canadian Sunbeam Lamp Company of Toronto. The equivalent argon pressure was 102.4 atmospheres, and as it was known from previous work that nitrogen at a pressure of 140 atmospheres was transparent in this region, the effect of the nitrogen in the tube was neglected. The photographic plates were Wratten panchromatic, as in the previous experiments and the time of exposure was one and three-quarters hours. There was no indication of any appreciable or visual absorption between the wave-lengths $\lambda = 7000 \text{ \AA.U.}$ and $\lambda = 2150 \text{ \AA.U.}$

IV. *Summary*

1. The absorption spectrum of ionized argon gas at pressures of 155, 5, and 2 mm. of mercury has been investigated between the wave-lengths $\lambda = 7000 \text{ \AA.U.}$ and $\lambda = 2150 \text{ \AA.U.}$ No absorption was detected.

2. The absorption spectrum of argon gas at an equivalent pressure of 102.4 atmospheres has been studied in the same region. The gas at this pressure has been found to be transparent between the wave-lengths previously mentioned.

In conclusion the author wishes to express his sincere thanks to the members of the Advisory Council for Scientific Research, and particularly to Professor J. C. McLennan, F.R.S., who suggested these researches and under whose direction they were carried out. The author also desires to express his gratitude to Miss M. L. Clark, who assisted in the purification of the gas and in filling a number of the tubes.

Physical Laboratory,
University of Toronto.
May 15th, 1922.

PLATE 2

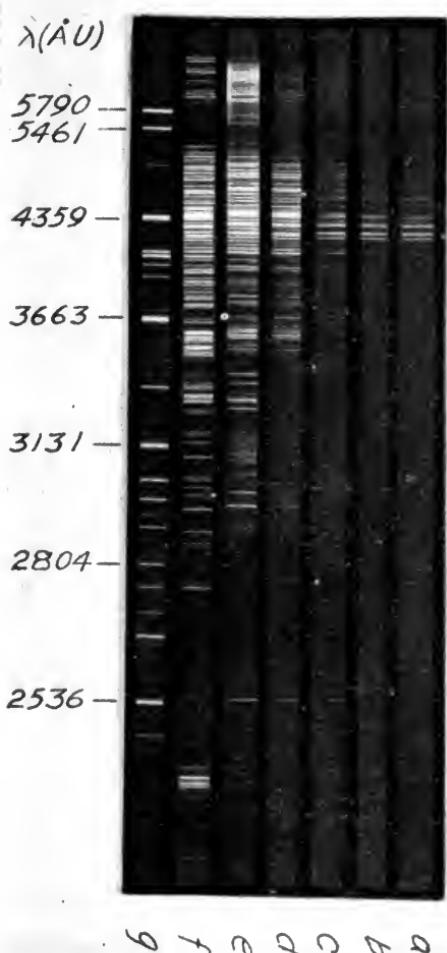
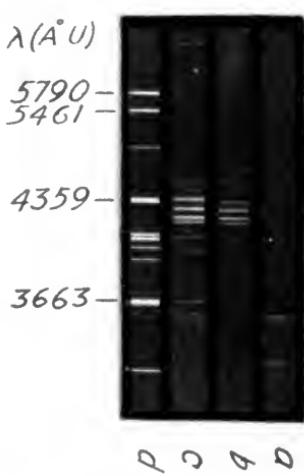
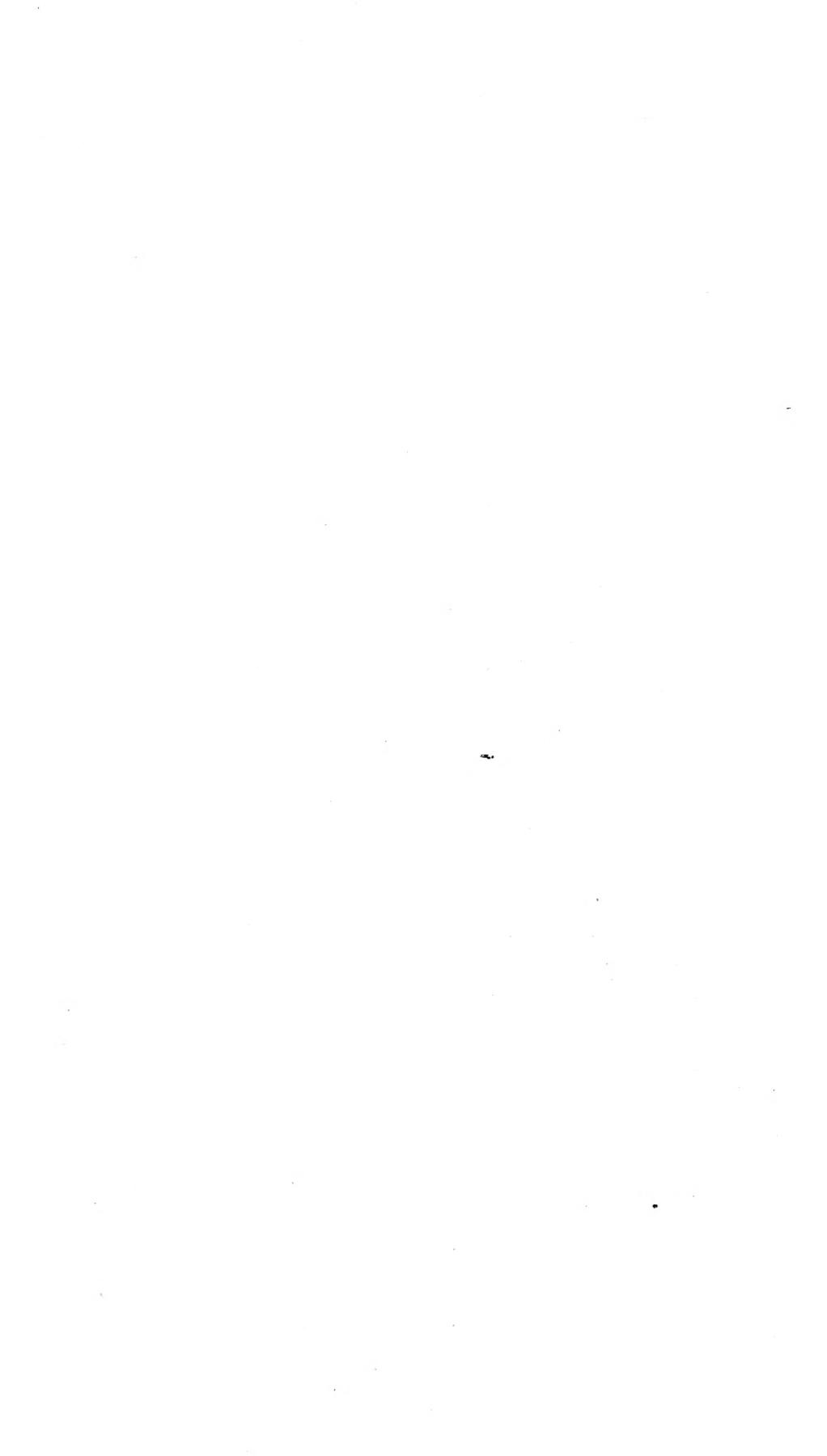


PLATE 1





[*From the* PROCEEDINGS OF THE ROYAL SOCIETY, A, VOL. 100, 1921.]

On the Emission and Absorption Spectra of Mercury.

By J. C. McLENNAN, F.R.S., AND W. W. SHAVER, M.A.

On the Emission and Absorption Spectra of Mercury.

By Prof. J. C. MCLENNAN, F.R.S., and W. W. SHAVER, M.A., University of
Toronto.

(Received June 29, 1921.)

[PLATE 7.]

1. *Introduction.*

In two papers by Raymond C. Dearle* accounts are given of investigations in which a special study was made of the monochromatic radiation $\lambda = 1\cdot014\mu$. This radiation Paschen† found to be by far the strongest in the emission arc spectrum of mercury, and Dearle's observations corroborated this view.

Dearle found moreover, that when light of this wave-length was passed through non-luminous mercury vapour, even when of low density, a definite and well-marked absorption was obtained. He also found the same effect when the mercury vapour traversed was in direct contact with the mercury vapour in which the arc was established from which the original radiation was obtained, and was also directly illuminated by the radiation from this arc.

It is well known that the radiations whose frequencies are given by $\nu = (1\cdot5, S) - (2, p_2)$, i.e., $\lambda = 2536\cdot72$ Å.U. and $\nu = (1\cdot5, S) - (2, P)$, i.e., $\nu = 1849\cdot6$ Å.U. are strongly absorbed by non-luminous mercury vapour, but no one as yet has been able to confirm the observations made by Dearle that the radiation $\nu = (2, P) - (2\cdot5, S)$, i.e., $\lambda = 1\cdot014\mu$ is absorbed by mercury vapour which is not luminous.

It is quite clear from the application of the quantum theory made by Bohr

* Dearle, 'Roy. Soc. Proc.,' A, vol. 92, p. 608 (1916); vol. 95, p. 280 (1919).

† Paschen, 'Ann. der Phys.,' vol. 27 (13), p. 559 (1908).

to the problem of the origin of radiation that if mercury vapour were illuminated by radiation of frequency $\nu = (1\cdot5, S) - (2, P)$, *i.e.*, $\lambda = 1849\cdot6 \text{ \AA.U.}$, a certain number of the atoms of mercury in the vapour would have the configuration of their constituent extra-nuclear electrons so modified that they would be in the condition to absorb the wave-length $\lambda = 1\cdot014 \mu$; but in the absence of illumination by radiation of the wave-length $\lambda = 1849\cdot6 \text{ \AA.U.}$, or of excitation of the mercury vapour by an equivalent stimulus, it is not clear how absorption of a radiation of the wave-length $\lambda = 1\cdot014 \mu$ by the mercury vapour could be obtained. If the effect observed by Dearle was correctly interpreted by him, it would mean that the atoms of ordinary mercury vapour would have in addition to the well-established resonance potential of 4·9 volts, corresponding to $\lambda = 2536\cdot72 \text{ \AA.U.}$, an additional one of 1·26 volts, corresponding to $\lambda = 1\cdot014 \mu$.

Although extensive investigations have been made on the resonance and ionisation potentials of many of the elements, there appears to be very little evidence obtainable from them which would go to support the suggestion put forward by Dearle that ordinary unexcited mercury atoms are really characterised by the two resonance potentials mentioned. Mercury atoms which have absorbed the radiation $\lambda = 1849\cdot6 \text{ \AA.U.}$ could, on the Bohr theory, possess the resonance potential 1·26 volts, but not mercury atoms whose electronic systems are in their ordinary stable configurations, provided views of the origin of radiations which are generally held at present remain valid.

As the suggestion put forward by Dearle as a result of his observations is of fundamental importance in connection with theories of atomic structure it was decided to set in train two lines of investigation with the object of clearing up the matter if possible. One of these investigations was undertaken by one of the authors of the present communication, and the second by the other. In the first investigation the photographic method was used, and in the other the method adopted involved the use of the spectrophotoelectric thalofide cell recently discovered by T. W. Case.*

In both of the investigations no evidence was obtained of any measurable absorption of radiation of the wave-length $\lambda = 1\cdot014 \mu$ by non-luminous mercury vapour. In the case of luminous mercury, however, an easily measurable absorption of radiation of this wave-length was obtained when a thalofide cell was used to measure the intensities of the radiation.

* T. W. Case, 'Phys. Rev.' [2], vol. 15, p. 289 (1920); also U.S. Patents Nos. 1301227 and 1316350 for a light reactive resistance,

THE PHOTOGRAPHIC METHOD, by Prof. McLennan.

1. *Infra-red Photography.*

From the recently published accounts of the brilliant investigations carried out by Meggars,* Kiess,† and Merrill,‡ it became abundantly clear that by the use of photographic plates stained with the dye dicyanin it was possible to photograph spectra as far as $\lambda = 11650 \text{ \AA.U.}$, and possibly beyond this limit.

As no photographs appeared to have been taken of the spectrum of mercury by these or other investigators with dicyanin-stained plates it appeared worth while attempting to take them. Considerable difficulty was experienced in obtaining dicyanin of good quality, but through the kindness of Dr. C. K. Mees of the Eastman Kodak Company some was finally obtained which enabled us to photograph spectra well up to the limit mentioned above.

2. *Photographic Results with Emission Spectra.*

Before proceeding to photograph the spectrum of mercury, it was considered best, in order to gain familiarity with the technique of the various operations, to make a study of the spectra of a number of the elements already investigated by Meggars and Kiess. In this work various types of plates were tried out, with both prism and grating spectrographs, the source of light being either a strong arc between metal electrodes or between carbon electrodes filled with salts of the various metals. In the case of mercury, ordinary commercial glass mercury-arc lamps, and also quartz mercury-arc lamps, were used.

With exposures up to six hours' duration, and a fairly fine spectograph slit, the limit of Wratten and Wainwright panchromatic plates with moderate exposures was found to be about $\lambda = 7000 \text{ \AA.U.}$, and that of Ilford red sensitive plates about $\lambda = 7500 \text{ \AA.U.}$ When ordinary rapid Seed dry plates, made by the Canadian Kodak Company, stained with dicyanin were used, spectra of moderate intensity were obtained, with a fine slit up to slightly over 10000 \AA.U. , with 12-17 hours' exposure. With a wide slit and 32 hours' exposure, spectra were obtained quite readily up to 11137 \AA.U. , with indications that in the case of very strong radiations this limit would be considerably extended.

The reproductions shown in (1), Plate 7, were obtained in photographing the

* Meggars, 'Bulletin of the Bureau of Standards,' vol. 14, p. 371 (1917).

† Kiess and Meggars, 'Bulletin of the Bureau of Standards,' No. 324, p. 637 (1918); and No. 372, p. 51 (1920).

‡ Merrill, 'Bulletin of the Bureau of Standards,' No. 318, p. 487 (1918).

spectrum of the mercury arc in the near infra-red, and those in (2), when an attempt was made to extend the spectrum of mercury as far into the infra-red as possible. In obtaining (1) a quartz mercury-arc lamp was used, which was operated with a current of about three ampères under a potential difference of about 40 volts. The slit used was wide, about $1\frac{1}{2}$ mm., and the exposure was about 32 hours. The spectrum was of the first order, the over-lapping portions of the higher orders being cut off by the use of a Wratten-Wainwright filter No. 22.

With the setting of the grating adopted in obtaining the spectrogram (a), (2), the wave-length $\lambda = 10140 \text{ \AA.U.}$ came, as the reproduction shows, somewhat near the end of the plate. A new setting of the grating was therefore made, which brought this wave-length somewhat more to the right of the plate. An exposure of 17 hours' duration was then made, with the lamp running under the same conditions as before, and with the same filter inserted. In this case, however, the slit was made about one-half as wide as it was in taking the first plate. The spectrogram obtained is that designated as "b," (2).

Reproduction "a," (2), shows that the radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$ came out as a strongly marked diffuse wide band. The over-exposure was, however, too great to bring out the actual structure of the band. The plate from which reproduction "b" was taken was rather under-exposed, but in the original $\lambda = 10140 \text{ \AA.U.}$, though faint, could be seen quite definitely, either as a band about 60 \AA.U. in width, with inversion at the centre over a range of about 20 \AA.U. , or a doublet with about 35 \AA.U. , or about 40 \AA.U. separation between centres. In the reproduction the detail is not clear. The fact, as the reproduction shows, that wave-lengths slightly above and slightly below $\lambda = 10140 \text{ \AA.U.}$ came out clearly on the plate, rather points in the direction of inversion.

In reproduction "c," (3), which will be referred to later, the detail came out more definitely than in either "a" or "b." There it will be seen there is a strongly marked band at $\lambda = 10217 \text{ \AA.U.}$, a less strongly marked one at $\lambda = 10165 \text{ \AA.U.}$, and a fainter and narrower one at $\lambda = 10121 \text{ \AA.U.}$ The latter two would appear to make up what has hitherto been taken to be the wave-length $\lambda = 10140$, and the existence of the third strong band close to them at $\lambda = 10217 \text{ \AA.U.}$ would account for the strongly marked diffuse wide band shown in "a."

On measuring up the spectrograms of the mercury spectrum, it was found that wave-lengths were obtained up to $\lambda = 11137 \text{ \AA.U.}$, a number being recorded which had not been observed. These are given in the list collected in Table I, and are considered to be correct to 1 \AA.U. The results obtained

by Wiedemann* and by Stiles,† which appear to be the most complete hitherto recorded in the range covered by the present observations, are also given in the Table.

Table I.—Wave-Lengths from Mercury Arc.

Relative intensities.	Observer.		
	The Author.	Wiedemann.	Stiles.
8	Å.U. 6908 —	A.U. 6907 '776 7044	A.U. 6907 '74 —
10	7082 '92	7082 '278	7081 '96
10	7092 '46 —	7092 '456 7122	
2	7179	7179	
1	7295	7295	
1	7371	7371	
2	7453	7453	
2	7551	7551	
2	7606	7606	
3	7678	7676	
8	7729 '46	7729 '456	
3	7821	7821	
2	7992	7982	
2	8028	—	
2	8077	8077	
1	8104	—	
1	8145	—	
3	8164	8164	
3	8198	8198	
1	8665		
1	8730		
1	8774		
1	8798		
1	8832		
1	9025		
1	9057		
3	9217		
3	9255		
3	9288		
1	9327		
1	9439		
1	9487		
1	9510		
1	9565		
1	9597		
1	9628		
1	9710		
1	9753		
2	9914		
2	9953		
2	9993		
2	10037		
2	10078		
30 {	10121 } 10140 10165		

* Wiedemann, 'Ann. der Phys.,' vol. 38, p. 1041 (1912).

† Stiles, 'Astrophysical Journal,' vol. 30, p. 48 (1909).

Table I—(*contd.*)

Relative intensities.	Observer.		
	The Author.	Wiedemann.	Stiles.
3	A.U. 10217	A.U.	A.U.
1	10301		
4	10344		
6	10377		
6	10416		
6	10453		
3	10485		
8	10581		
2	10567		
1	10845		
1	10874		
1	10883		
4	11053		
4	11088		
4	11101		
4	11137		

It will be seen that, in all, some forty-four new wave-lengths in the spectrum of mercury have been identified photographically. Of these, $\lambda = 1.038 \mu$ and $\lambda = 1.045 \mu$, respectively, had been previously observed by McLennan and Dearle,* and by Moll,† with a radiometric method involving the use of a linear thermocouple.

It may be that some of the wave-lengths given in the list are merely ghosts, for, in taking spectrograms with the same grating in the visible region, several of the strong lines in the spectrum of mercury were accompanied by them. Apart from this possible defect, however, the results are interesting, as showing that the wave-lengths of the radiation emitted by a luminous mercury vapour can be photographically recorded at least as far as $\lambda = 11137 \text{ \AA.U.}$, and that we have in this way a new means of investigating the character of such important radiations as $\lambda = 10140 \text{ \AA.U.}$, and of studying their specific properties.

3. Absorption Experiments.

In carrying out the absorption experiments, the procedure followed and the optical arrangements made, were, with one exception, identical with those adopted in obtaining the photograph of the emission spectrum of mercury, shown in reproduction "a," (2). The exception mentioned

* McLennan and Dearle, 'Phil. Mag.', vol. 30, November, 1915, p. 683.

† Moll, 'Kon. Akad. Wet. Amsterdam, Proceedings,' vol. 9, p. 544 (1907).

consisted in the insertion of a highly exhausted glass tube, 2·5 cm. in diameter, immediately in front of the slit.

A photograph was taken of thirty-two hours' duration, with this tube partly filled with mercury, and heated by an electric furnace to 300° C. In this case the tube was adjusted in position, so that the surface of the mercury was just below the bottom of the slit. At the temperature used it will be seen that the density of the mercury vapour traversed by the light was at least as high as that used in the experiments by Dearle.

A reproduction of part of the plate obtained in this case is shown in "c," (3). Accompanying it there is shown the corresponding portion of reproduction "a," (2). Through some stray light reaching it, either when in the spectrograph or in the developing room, the plate was slightly covered with a thin fog. It shows, however, quite definitely the wave-length $\lambda = 10140$. It is true this wave-length does not come out as a strongly marked broad band as in "a," but the difference was no doubt due to a part of the impinging light being reflected from or absorbed by the glass walls of the absorption tube.

It seems clear from the reproduction that there was little, if any, absorption by the mercury vapour in the absorption tube. If any absorption by the vapour did take place, it was extremely small compared with what one readily obtained with radiation of wave-lengths $\lambda = 2536\cdot72$ Å.U. and $\lambda = 1849\cdot6$ Å.U. It is true that the absorption of $\lambda = 10140$ Å.U. obtained by Dearle with non-luminous mercury vapour was only partial, but it was sufficiently well defined, according to his curves, to expect some indication of it on our photographic plates, if what he observed was a real absorption effect.

In so far, then, as these experiments go, they show that non-luminous mercury vapour does not absorb the radiation $\lambda = 10140$ Å.U. to the extent of appreciably weakening the photographic record of this wave-length.* It would follow, then, that mercury atoms, with their electronic systems in their ordinary undisturbed state, do not have a resonance potential of 1·26 volts, and that therefore the true resonance potential for mercury atoms is the well established one, and corresponding to the quantum equivalent of $\lambda = 2536\cdot72$ Å.U., *i.e.*, to about 4·9 volts.

A number of wave-lengths were recorded on "c," (3), which were not strongly marked on either "a" or "b" of (2). Their values are given on the plate, and are also included in the list given in Table I.

* From a note in 'Nature' of April 14, 1921, p. 203, the writer has just learned that the spectrum of mercury vapour has been recently photographed by A. Terenin up to $\lambda = 11300$ Å.U. In this investigation there was found no absorption by non-luminous mercury vapour of the radiation of wave-length $\lambda = 10140$.

The writer wishes to take this opportunity of expressing his appreciation of the help he received in making the optical arrangements, and in taking the photographs, from his research assistant, Mr. Vladimir Lubovich, of the University of St. Petersburg.

Thalofide Cell Experiments. By W. W. SHAVER.

1. *The Cell and its Properties.*

The thalofide cell used in these experiments was invented by and obtained from T. W. Case,* of the Case Research Laboratory, Auburn, New York. The active part of this cell is a preparation of thallium-oxy-sulphide, fused on the surface of a quartz plate, the latter being securely mounted within an evacuated cylindrical glass flask, about 2·5 cm. in diameter. Evacuation was found to increase the sensitivity of the cell and to prevent deterioration through oxidation. The cell is photo-electrically sensitive in the near infra-red region from $\lambda = 6000 \text{ \AA.U.}$ to $\lambda = 12000 \text{ \AA.U.}$ The sensitivity curve, as given by Coblenz,† shows a sharp rise from $\lambda = 6000 \text{ \AA.U.}$ up to $\lambda = 9000 \text{ \AA.U.}$, and then a further rise to $\lambda = 10000 \text{ \AA.U.}$ From this wave-length on the sensitivity falls off rapidly, and is practically *nil* at 12000 \AA.U. .

The photo-electric sensitivity of this cell consists in a lowering of the electric resistance of the active preparation when it is exposed to radiations comprised within the limits mentioned. As the cell has its maximum sensitivity at or near $\lambda = 10000 \text{ \AA.U.}$, it was thought that it might prove specially suitable for studying radiation from mercury vapour of wavelength $\lambda = 10140 \text{ \AA.U.}$, and some preliminary experiments showed this conjecture to be well warranted.

The following is a short account of some experiments involving the use of this thalofide cell, and arranged with the object of investigating whether or not $\lambda = 10140 \text{ \AA.U.}$ is absorbed by non-luminous and by luminous mercury vapour. It may be stated here that the results of the investigation go to show that $\lambda 10140 \text{ \AA.U.}$ is not appreciably absorbed by non-luminous mercury vapour, but that it is absorbed to a marked extent by mercury vapour in which an arc of low intensity is maintained.

2. *Sensitivity Measurements.*

In commencing the investigation, some observations were made on the sensitivity of the cell when activated by light from a carbon-filament incandescent lamp, and by that from a quartz mercury arc lamp. Following

* Case, 'Phys. Rev.', 1920, p. 289.

† Coblenz 'Bureau of Standards,' Washington, No. 380, p. 253 (1920).

the instructions given by Paschen,* Wratten filters Nos. H. 45 and F. 29, together with a water cell 1 cm. in thickness, were used to confine the light falling on the cell to the range of wave-lengths lying between $\lambda = 8500 \text{ \AA.U.}$ and $\lambda = 15000 \text{ \AA.U.}$ As the sensitivity of the cell is practically zero for $\lambda = 12000 \text{ \AA.U.}$, this arrangement resulted in the effective wave-lengths being necessarily limited to those between $\lambda = 8500 \text{ A.U.}$ and $\lambda = 12000 \text{ \AA.U.}$ Within this range the radiation of wave-length $\lambda = 10140$ is, according to the observations of Dearle, by far the strongest in the light emitted by the mercury arc, and consequently in what follows it has been assumed that the effects obtained when the light from the mercury arc was used may be considered as being ascribable to the radiation $\lambda = 10140 \text{ \AA.U.}$ In these experiments, with a carbon filament lamp of 32 candle-power, and a mercury-arc lamp, the former was placed at a distance of about 132 cm., and the latter at a distance of about 40 cm., from the active surface of the cell. The cell was joined in a series with a resistance of 240,000 ohms, a Tinsley galvanometer of 4000 ohms resistance and a storage battery having a potential difference of 4.72 volts. Readings were taken in millimetres on a scale at a distance of 1 metre from the galvanometer, and the sensitivity of the latter was such as to give 240 mm. deflection at 1 metre per microampère.

The unilluminated thalofide cell was found to give with this circuit a steady so-called "dark current" of 135 mm. deflection, but when the cell was illuminated this deflection was increased by an amount which depended on the intensity of the activating radiation as determined by the energy consumed by the source. Tables I and II contain the values of these added deflections, together with the corresponding amounts of energy supplied to the lamps.

Table I.—Carbon Filament Lamp.

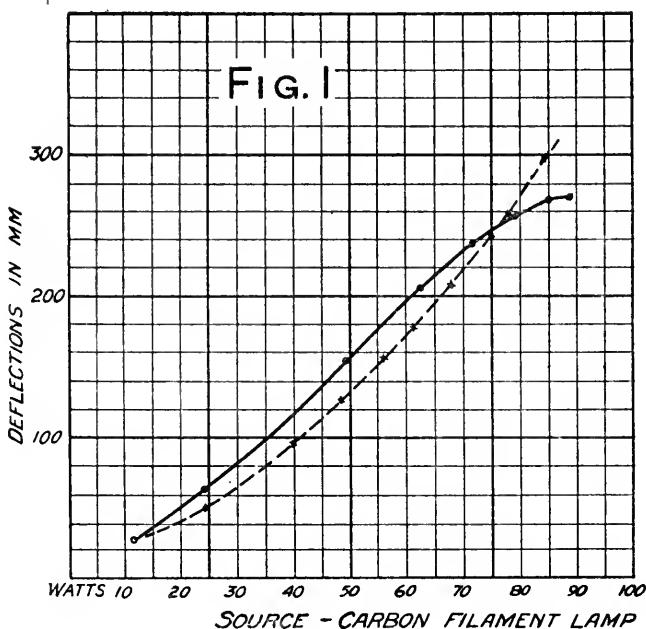
Source energy. watts.	Increase in galvanometer deflection. mm.	Source energy. watts.	Increase in galvanometer deflection. mm.
89.4	267	39.9	98
85.1	267	47.9	126
79.2	256	56.6	157
72.2	238	61.2	178
63.4	205	67.6	208
49.9	155	75.3	242
24.4	63	77.9	259
11.2	27	84.3	295
24.1	51		

* Paschen, 'Wied. Ann.', No. 43, p. 858 (1914).

Table II.—Mercury Arc Lamp.

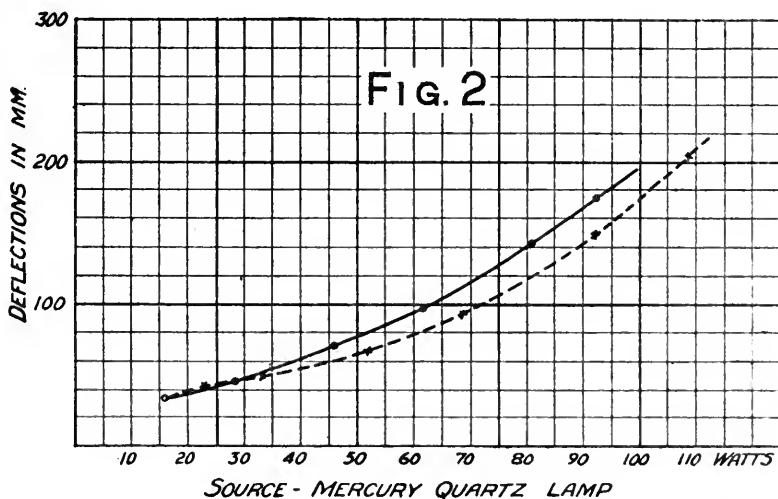
Source energy. watts.	Increase in galvanometer deflection. mm.	Source energy. watts.	Increase in galvanometer deflection. mm.
110.0	164	16.0	37
123.2	232	23.0	43
92.5	174	33.0	50
80.5	143	51.3	68
62.4	97	68.7	94
45.5	71	92.0	147
28.6	48	108.1	205

In figs. 1 and 2 graphs are drawn corresponding to the numbers in the Tables, the continuous curve representing the deflection obtained with a decreasing supply of energy and the broken one representing those obtained as the energy supplied to the lamp increased.



As the cell did not reach a steady state at once when being exposed to the radiation, all the readings were taken one minute after the commencement of each exposure. The lag shown by the curves was obtained when both lamps were used, and although it is known that it takes a considerable time for the quartz mercury arc lamps to settle down into a steady state after they are set in operation, it is thought that sufficient time was allowed after starting the

lamp for the steady state to be reached and that, therefore, the lag observed should be connected up, in the main, with the functioning of the thalofide



cell. From the values given in the Table it will be seen that under illumination an increase in current was easily obtained of twice the amount of the original "dark current."

3. Preliminary Absorption Experiments.

In these experiments the quartz mercury arc lamp was used as the source of radiation and the thalofide cell was provided with the filters mentioned in Section 2, the light being admitted to the cell through a slit about 2·5 mm. in width. When the lamp had reached a steady state and the galvanometer in series with the thalofide cell showed a steady deflection due to the illumination of 136 mm., an empty thin-walled pyrex glass bulb about 9 cm. in diameter was placed between the lamp and the filters. This produced a drop in the galvanometer deflection of 22 mm., due to reflection from or adsorption by its walls. A quantity of mercury was then placed in the bulb which was afterwards exhausted, hermetically sealed, and as previously, placed in the same position in the path of the light, care being taken to see that no mercury adhered to the walls of the bulb. In this case the fall in deflection due to the insertion of the bulb was practically the same as that obtained when it was empty. Heat was next applied to the bulb by means of an electric furnace and at the same time the walls of the bulb at the points of entrance and exit of the light were heated directly with auxiliary Bunsen burners, in order to prevent any deposit taking place from the mercury vapour. This was found to be necessary as it was observed that even a slight and scarcely

visible deposit of condensed vapour on the bulb walls immediately produced a marked decrease in the galvanometer readings.

In one particular set of readings with the mercury bulb at 24° C. an added deflection due to illumination of 151 mm. was obtained. When the bulb was heated to 350° C. the added deflection obtained was 152.5 mm. The consumption of energy by the lamp was checked during heating and it was found not to vary more than 1 per cent. From this it seemed clear that practically no absorption of the illuminating radiation took place. As mentioned above, the active radiation was confined to wave-lengths between $\lambda = 8500 \text{ \AA.U.}$ and $\lambda = 12000 \text{ \AA.U.}$, and as $\lambda = 10140 \text{ \AA.U.}$ was in all probability the most intense radiation in this range it seemed fair to conclude from these experiments that this wave-length was not appreciably absorbed by non-luminous mercury vapour.

4. *Absorption Experiments with Non-luminous Mercury Vapour.*

(a) A series of experiments was then made with the activating radiation confined entirely to the wave-length $\lambda = 10140 \text{ \AA.U.}$. With the grating used in the experiments described in the first part of this paper, it was possible to locate with precision from measurements on the photographic plates, the exact position of $\lambda = 10140 \text{ \AA.U.}$. The thalofide cell was therefore mounted in a tube attached to a plate which fitted into the grooves of the plate holder so that it could be moved along the focal plane of the grating. The slit of the spectrograph was widened to about 1.5 mm., and a second slit of 4 mm. width was placed immediately in front of the thalofide cell to limit the radiation which could enter the latter from the grating. The light from a mercury arc lamp was projected on the slit of the spectrograph after passing through a Wratten filter No. 22, inserted to cut off the green, violet and ultra-violet radiation of the second order spectrum. The plate carrying the thalofide cell was then moved along the grooves in the focal plane to the point previously determined as the position of the focussed radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$. As soon as this position was reached, a large increase in the galvanometer deflection was at once obtained, and it was interesting to observe how accurately this wave-length could be located by the use of the thalofide cell. Movements of the latter in the focal plane in either direction were immediately followed by the disappearance of the galvanometer deflection in excess of that due to the "dark current."

When it was found that large readings could be readily obtained with the thalofide cell when the radiation was limited to the wave-length $\lambda = 10140 \text{ \AA.U.}$, an experiment was made to test the absorption of this particular wave-length by non-luminous mercury vapour.

The pyrex glass mercury vapour absorption tube used in the photographic experiments was mounted in the electric furnace and placed in front of the spectrograph slit in the path of the light from the mercury arc. This produced a drop in the galvanometer deflections of 30 mm., when the reading due to the direct radiation was 105 mm. The tube was then heated to 300° C., and the galvanometer readings were noted as the temperature of the vapour tube rose. No difference was observed in the galvanometer readings, the deflection being still 75 mm. when the temperature of 300° C. was reached. At this temperature it will be noted that the density of the mercury vapour was that corresponding approximately to atmospheric pressure. This experiment was repeated with a 300-watt argon-filled tungsten lamp as the source of radiation, and in this case also no absorption by the mercury vapour was observed.

(b) To make a more exacting test for absorption than that made in the previous experiment, two absorption tubes of pyrex glass, of exactly the same dimensions, 24·4 em. in length and 2·5 cm. in diameter, were constructed with plane parallel plate windows cut from the same sheet of glass. Some mercury was put into one of the tubes, and then both were highly exhausted and hermetically sealed. The windows of the mercury tube were kept absolutely free from condensed vapour by being gently warmed by a heating circuit of nichrome wire wound about the two ends. The mercury absorption tube was mounted between the source of radiation and the spectrograph slit in such a way that it could readily be removed and the empty tube placed in an exactly similar position. Having obtained the "dark current" galvanometer deflection, the light from the source was allowed to fall on the spectrograph slit, after passing through the absorption tube. The increase in galvanometer deflection was noted as soon as it became steady, and then the empty tube was quickly substituted for the absorption tube. The deflection was again taken, and in this way any change of galvanometer deflection due to the absorption of the radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$ by the mercury vapour could be determined immediately..

The following Tables give the results of a series of pairs of readings, using both the mercury-arc and the argon-filled tungsten lamp as sources of the radiation $\lambda = 10140 \text{ \AA.U.}$

From the Table it will be seen that when the mercury-arc lamp was used as the source of the radiation $\lambda = 10140 \text{ \AA.U.}$, the average of the readings obtained with the empty tube was the same as that of those obtained with the tube which had the mercury in it. When the tungsten lamp was used as the source of the radiation, practically the same result was obtained, as

the slight difference in the mean of the readings for the two tubes (0·4 per cent.) was well within the limits of experimental error.

Table III.—Mercury-Arc Lamp.

Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through		Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through	
(a) Mercury absorption tube.	(b) Empty tube.	(a) Mercury absorption tube.	(b) Empty tube.
mm.	mm.	mm.	mm.
64	65	66	68
64	64	61	59
66	65	59	56
63	63	—	—
62	63	70	69
58	58	70	75
—	—	69	69
66	65	67	69
70	70	69	66
70	70	59	61
70	69		
Mean	69·1	69·1

Table IV.—Tungsten Lamp.

Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through		Increase in galvanometer deflection when radiation of wave-length 10140 Å.U. was passed through	
(a) Mercury absorption tube.	(b) Empty tube.	(a) Mercury absorption tube.	(b) Empty tube.
mm.	mm.	mm.	mm.
134	137	144	138
144	136	130	137
137	137	130	135
135	137	141	132
139	136	132	135
Mean	136·6	136·0

This experiment, therefore, makes it very clear that the radiation $\lambda = 10140 \text{ \AA.U.}$ is not absorbed to any appreciable extent by mercury vapour saturated at room temperature.

(c) A third experiment was made to test the absorption of $\lambda = 10140 \text{ \AA.U.}$ by saturated mercury vapour of various densities. The sources of the

radiation were again the quartz mercury-arc lamp and the tungsten argon-filled one. The absorption tube was the one referred to in "(b)," which contained some mercury. This tube was placed within an electric furnace, whose temperature was gradually raised to 350° C. Over this range of temperatures several sets of readings were taken with each of the lamps. A set of readings, taken with the mercury-arc lamp, as the source of the radiation $\lambda = 10140 \text{ \AA.U.}$ is given in Table V, and a set taken with the tungsten lamp is given in Table VI.

Table V.—Mercury-Arc Lamp.

Temperature of tube.	Increase in galvanometer deflection over that due to "dark current."	Temperature of tube.	Increase in galvanometer deflection over that due to "dark current."
° C. 25 65 105 130 150 165 178 203 219	mm. 71 86 74 78 86 76 82 76 83	° C. 233 245 257 266 293 295 320 325 350	mm. 76 76 76 69 79 86 74 78 78

Table VI.—Tungsten Lamp.

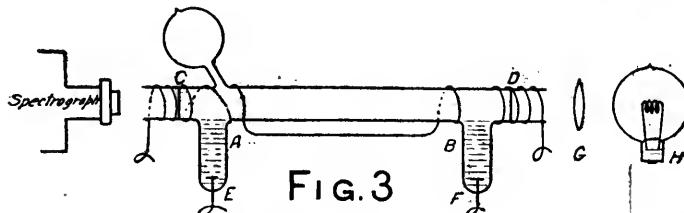
Temperature of tube.	Increase in galvanometer deflection over that due to "dark current."	Temperature of tube.	Increase in galvanometer deflection over that due to "dark current."
° C. 22 28 40 58 78 103 117 138 155 171	mm. 135 140 138 135 138 136 136 136 138 141	° C. 187 203 211 225 240 260 290 320 350	mm. 141 139 138 136 134 134 132 138 135

It will be seen that there was some irregularity in the readings given in the previous Tables, particularly when the mercury arc was used as a source of the radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$ This was due to unsteadiness in the voltage from the current supply mains, and in the case of the mercury-arc it was also caused by variations in the energy consumption of the lamp itself. However, from these readings it is clear that as the vapour density increased up to that corresponding to a pressure of one atmosphere,

there was, on the whole, no decrease in the galvanometer deflections. This showed that the amount of radiation of wave-length 10140 \AA.U. coming from the source through the absorption tube, was independent of the density of the mercury vapour in the tube, and therefore that the non-luminous mercury vapour did not absorb the radiation of this wave-length.

5. Absorption Experiments with Luminous Mercury Vapour.

In order to see whether luminous mercury vapour would absorb radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$, a lamp A B, shown in fig. 3, was made up out



of pyrex glass. The ends of this lamp were closed by two sealed-in plane parallel plates of pyrex glass, as shown in the diagram. The lamp was partly filled with mercury as indicated, and it was then evacuated and sealed up. By means of two auxiliary heating coils the end-plates at C and D were kept hot and therefore free of any deposit from the mercury vapour. This lamp was placed before the slit of the spectrograph, as shown in the diagram, and the light from the source, H, containing radiation of the wave-length $\lambda = 10140 \text{ \AA.U.}$ was focussed with the lens, G, on the slit after passing through the lamp A B. The thalofide cell as in the previous experiments was joined in series with a battery, a galvanometer and a high resistance, and was mounted in the focal plane of the grating so as to receive only the radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$. In these experiments, as in those previously described, the quartz mercury arc lamp and the tungsten lamp were used as sources of this radiation.

Readings were taken (1) of the "dark current" deflection when neither the source of light, H, nor the lamp, A B, were in operation; (2) when the pyrex lamp, A B was running with current just sufficient to maintain the arc; (3) when both the lamps, H and A B, were in operation; and (4) immediately after the arc in the pyrex lamp, A B, was extinguished, but while the source of light, H, was kept operating. From these readings it was possible to calculate the percentages of the radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$ from the source, H, absorbed by the vapour in the lamp, A B, when the latter was in the luminous state.

A summary of the results obtained from a number of these sets of readings is given in Table VII.

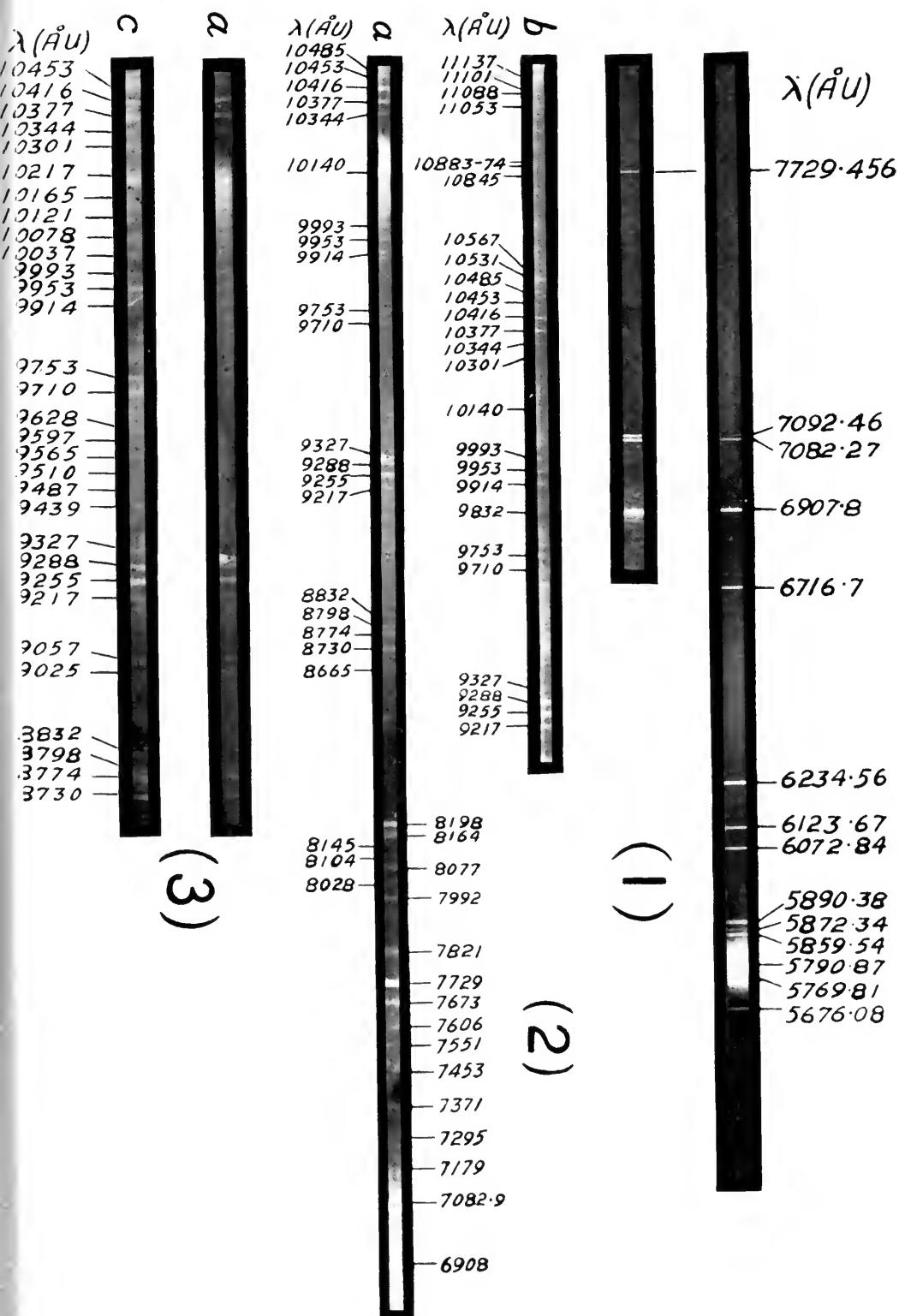


Table VII.

Source of radiation of wave-length $\lambda = 10140 \text{ \AA.U.}$	Increase in deflection over the "dark current" galvanometer deflection due to			Percentage absorption.
	Light from pyrex lamp, mercury arc.	Light from pyrex lamp, mercury arc, and from source II after passing through luminous vapour in A B.	Light from source II after passing through non- luminous vapour in A B.	
Quartz mer- cury arc lamp	Column I. (mm.)	Column II. (mm.)	Column III. (mm.)	Column IV.
	28.5	109.0	98.0	17.9
	26.0	101.0	92.0	18.5
	28.5	100.5	90.5	18.2
	28.0	86.0	76.0	23.7
Tungsten lamp	Mean			19.6
	11.0	128.0	124.0	5.6
	15.5	141.5	136.5	7.7
	18.0	124.0	120.0	7.5
	20.5	188.5	178.5	6.4
Mean				6.8

In calculating the percentage absorption given in column IV, the readings in column II were subtracted from the sum of the corresponding ones in columns I and III. These differences were divided by the corresponding numbers in column III, and were taken as measures of the fractional absorptions of the radiation by the luminous vapour. From these fractions the percentage absorptions easily followed.

These experiments are interesting examples of the use of thalofide cells, and they will serve to indicate the advantages which are likely to accrue from the extensive use of these cells in the future as radiometers, when measurements of intensity are required to be made in the near infra-red region.

6. Summary of Results of both Investigations.

(1) With plates stained with the dye dicyanin, the spectra of a number of the elements have been photographed in the infra-red region. In the case of mercury, the spectrum was photographed up to $\lambda = 11137 \text{ \AA.U.}$

(2) By the photographic method, as well as by the use of thalofide cells, it has been shown that non-luminous mercury vapour does not absorb radiation of the wave-length $\lambda = 10140 \text{ \AA.U.}$

(3) It has been found that slight and scarcely visible deposits of mercury vapour markedly absorb radiation of the wave-length $\lambda = 10140 \text{ \AA.U.}$, and this result may possibly afford an explanation of the observations made by Dearle,

(4) By the use of thalofide cells and low-intensity mercury arcs, it has been shown that radiation of the wave-length $\lambda = 10140$ Å.U. may be strongly absorbed by luminous mercury vapour.

(5) From the absence of absorption of radiation of wave-length $\lambda = 10140$ Å.U. by non-luminous mercury vapour, it follows that the atoms of mercury in their ordinary state do not possess a resonance potential of 1.26 volts, corresponding to $\lambda = 10140$ Å.U., in addition to the well-established one of 4.9 volts, corresponding to $\lambda = 2536.72$ Å.U.

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ON THE ABSORPTION SPECTRUM OF LIQUID AND
GASEOUS OXYGEN

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On the Absorption Spectrum of Liquid and Gaseous Oxygen

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(Presented by PROFESSOR J. C. McLENNAN, F.R.S.)

(Read May Meeting, 1921)

I. INTRODUCTION

An investigation was recently undertaken by the author to determine the effect of radiation of various wave lengths on gases, with special reference to hydrogen and nitrogen. During the course of this investigation it was thought some useful information on experimental conditions might be gained by a study of the analogous problem with oxygen, as the effect of radiation on this gas, particularly that in the ultraviolet region, is well-known, having been studied by a number of experimenters.

Accordingly some experiments were performed to obtain the absorption spectrum of oxygen, both in liquid and gaseous form, and in the photographs taken some bands were observed which apparently have not been previously recorded. The absorption spectrum of oxygen has been studied by Liveing and Dewar¹, Olszewski,² and others, who found that with a pressure of 85 atmospheres there were a number of bands in the visible region and a general absorption in the ultraviolet beginning about the wave-length $\lambda = 2745 \text{ \AA.U.}$, with complete absorption below the wave-length $\lambda = 2665 \text{ \AA.U.}$. When the pressure was increased to 140 atmospheres the bands in the visible were intensified while the ultraviolet absorption was complete below the wave length $\lambda = 2704 \text{ \AA.U.}$. In the experiments described in this paper seven bands have been observed in the visible region with the addition of four broad bands in the ultraviolet adjacent to the region of complete absorption. In the case of liquid oxygen eight bands were detected in the visible and the same broad ultraviolet absorptions, but the latter were not so sharply defined as with the gaseous oxygen. When these broad absorption bands were closely examined it was found that each one consisted of a set of finer triplet absorption bands. A brief description of the method of obtaining the photographs and also some further experiments which go to show that these bands were not due either to ozone or to impurity in the gas is given in the following.

¹ Liveing and Dewar, Phil. Mag. 26, p. 387, 1888; Phil. Mag. (5), 34, p. 205, 1892.² Olszewski, Wiedem. Ann., 42, p. 663, 1891.

II. ABSORPTION SPECTRUM OF LIQUID OXYGEN

In these experiments the light from the spark between aluminium terminals under water, after the manner devised by Henri,¹ was used as the source of radiation. The electrical arrangement for the production of the Henri spark is shown in Fig. 1. (See page 14).

The secondary terminals of an induction coil A B were joined to the spark gap C D and then to two condensers E, F, each of which consisted of two one-gallon Leyden jars joined in parallel, the wires from the secondary terminals being connected to the outside coatings of the two sets of jars as shown in the diagram. The inside coatings of the jars were then joined to a second spark gap consisting of aluminium rods, G, H, about 1 cm. in diameter and conically pointed. These rods were mounted in a vertical plane inclined to each other at an angle of about 45° and held in position by clamps which were provided with threads so that the distance between the sparking points could be readily adjusted. These aluminium terminals were immersed to a depth of about 5 cm. in distilled water in a metal vessel provided with a quartz plate window about 2 cm. in diameter and placed at the proper height so that the spark occurred immediately in front of the window. The light from the spark was focussed by a cylindrical quartz lens on the slit of the spectrograph which was of the large quartz type made by the Adam Hilger Co. Several photographs of the spectrum of this light were taken and it was found to be almost perfectly continuous from the wave length $\lambda = 7000 \text{ \AA.U.}$ to the wave-length $\lambda = 2150 \text{ \AA.U.}$, as there were only two very slight aluminium reversals throughout this entire range.

The absorption spectrum of liquid oxygen in the visible region was obtained by passing the light from the spark between the aluminium terminals under water through a column of liquid oxygen contained in a cylindrical glass Dewar flask about 5 cm. in internal diameter. The flask was specially prepared for this purpose by being only partly silvered so that there was a clear slit about 1 cm. in width through which the light could pass. A reproduction of the photograph obtained is given in Plate I, Fig. 2 (b), in which there can be seen eight well-marked absorption bands. The mean wave-lengths of these bands were measured and the results are given in Table I, together with the wave lengths of the absorptions obtained by Liveing and Dewar, and Olszewski.

The absorption spectrum in the ultraviolet region was readily obtained by the use of a small cylindrical Dewar flask, about 1.8 cm.

¹ Henri, Phys. Zeit., No. 12, p. 516, June 15th, 1913.

in diameter, made of clear fused quartz which easily transmitted radiation down to the wave length $\lambda = 2150 \text{ \AA.U.}$. This flask was mounted in front of the slit of the spectrograph and filled with liquid oxygen. As before, the light from the spark between aluminium terminals under water was used as the source of radiation and some well-defined broad absorption bands were obtained in the region bordering that of complete absorption. These broad bands were about 30 \AA.U. in width, and within each one a fine set of symmetrical triplet bands could be distinguished. The reproduction of the photograph taken, which is given in Plate I, Fig. 3 (b), shows the broad absorptions but the sets of triplet bands are not so evident. However, it was found possible to measure the wave lengths of the component bands in three of these sets, and these results, together with the wave-lengths of the broad bands, are given in Table II. The first column contains the limits of the broad bands, the second their mean wave-lengths, and the last gives the mean wave-lengths of the three sets of fine bands.

TABLE I

Absorption by Liquid Oxygen

Author	Liveing and Dewar	Olszewski
Å.U. 6285	Å.U. 6300	Å.U. 6280
■ 5800	5775	5770
5350	5320	5350
4816		4800
4458	4433	
3828		
3631		
3461		

TABLE II

Absorption by Liquid Oxygen

Limits of Broad Bands	Means of Broad Bands	Means of Narrow Bands
2811 }	2795	
2780		
2747 }	2731	{ 2744 2731 2719
2716		{ 2692 2681
2694 }	2681	{ 2681 2670
2668		{ 2642 2632
2644 }	2631	{ 2632 2621
2618		

III. ABSORPTION SPECTRUM OF GASEOUS OXYGEN

The absorption chamber for this experiment consisted of a brass tube 35 cm. long and 2.5 cm. in diameter, threaded at each end so that the brass holders which supported the windows could be securely screwed on, making gas-tight joints. The windows were made of

plane parallel clear quartz plates, 1.2 cm. in thickness, and were firmly mounted and waxed in the brass holders mentioned above. Oxygen at a pressure of 140 atmospheres was passed into this tube which was then placed so that the light from the Henri spark passed through the absorbing column of oxygen into the slit of the same Hilger quartz spectrograph as was used before. The spectrogram obtained showed seven bands in the visible region which, as other observers have found, corresponded to the absorption bands obtained with liquid oxygen, although they were not so well marked. A reproduction of the photograph is shown in Plate I, Fig. 2(a), while the mean wave-lengths of the bands, together with those observed by Liveing and Dewar, are given in Table III.

In the ultraviolet region a broad band absorption, similar to that obtained in the case of liquid oxygen, was found (shown in Fig. 3 (a)), but with this difference, however, that each band was shifted slightly towards the ultraviolet. The bands were again about 30 Å.U. in width, and as before, each consisted of a fine set of symmetrical triplet bands which, in this case, were much more sharply defined, as the reproduction shows. The wave-lengths of the absorption bands were calculated and the results, given in Table IV, are tabulated in the same manner as those in Table II.

TABLE III

Absorption by Oxygen at 140 Atmospheres Pressure	
Author	Liveing and Dewar
A.U. 6285	Å.U. 6305
5800	5785
5350	5350
4816	4773
3828	4470
3631	
3461	

TABLE IV

Absorption by Oxygen at 140 Atmospheres Pressure		
Limits of Broad Bands	Means of Broad Bands	Means of Narrow Bands
Å.U. 2808	Å.U. 2790	Å.U.
2771		
2744	2729	2740
2714		2727
2692	2678	2716
2664		2687
2642		2677
2616	2629	2666
		2640
		2629
		2618

¹ Liveing and Dewar, loc. cit.

The experiment was repeated with the absorption tube filled with oxygen at 107 atmospheres pressure. In this case several of the bands in the visible region disappeared, leaving only the three strong bands with wave-lengths $\lambda = 6285 \text{ \AA.U.}$, $\lambda = 5800 \text{ \AA.U.}$, and $\lambda = 4816 \text{ \AA.U.}$, while the ultraviolet bands remained practically unchanged.

IV. INVESTIGATION OF THE ORIGIN OF THE SETS OF FINE ABSORPTION BANDS IN THE ULTRAVIOLET

(a) An experiment was performed to determine whether or not the sets of triplet absorption bands in the ultraviolet were due to some impurity in the gaseous or liquid oxygen used. The oxygen gas was guaranteed by the manufacturer to be 98% pure with nitrogen as the impurity, while liquid nitrogen was the most likely impurity in the liquid oxygen. The absorption of nitrogen was, therefore, tried out by using the apparatus described in Section III and passing nitrogen gas into the absorption tube at a pressure of 140 atmospheres. The experiment was performed in the same manner as when the absorption of oxygen gas was obtained, using the spark between aluminium terminals under water as the source of radiation. A photograph was taken of the absorption spectrum of nitrogen, but there was no trace of any absorption whatever showing that the bands obtained with oxygen as the absorbing medium were not due to the nitrogen impurity present.

(b) It was known from the work of W. N. Hartley,¹ and also E. Meyer,² that ozone strongly absorbs radiations between the wave-lengths $\lambda = 2850 \text{ \AA.U.}$, and $\lambda = 2330 \text{ \AA.U.}$, and it was thought that a small percentage of ozone might be present in the oxygen causing the band absorption which had been observed. This was the more probable on account of the narrow band absorptions obtained by Professors Fowler and Strutt³ in the region between the wave-lengths $\lambda = 3432.2 \text{ \AA.U.}$ and $\lambda = 3089.5 \text{ \AA.U.}$, using less than 1 per cent. of ozone in oxygen, as it was thought that with a smaller percentage of ozone some bands might appear farther down in the ultraviolet which would account for the absorption bands described in this paper. It has been shown by Regener⁴ and other observers that light of wave-length $\lambda = 1200 \text{ \AA.U.}$ to $\lambda = 1800 \text{ \AA.U.}$ is a powerful

¹ Hartley, Chem. News, p. 268, Nov. 26, 1880.

² Meyer, Ann. der Phys., Vol. XII, p. 849, 1903.

³ Fowler and Strutt, Proc. Roy. Soc. of London, 93, p. 577, 1916-17.

⁴ Regener, Ann. der Physik., 20, p. 1033, 1906.

ozonizing agent and that light of wave-length between $\lambda = 2300 \text{ \AA.U.}$ and $\lambda = 2900 \text{ \AA.U.}$ has an equally effective decomposing effect. It was thought that some weak radiation of wave-length approaching that necessary to produce ozone might be emitted by the spark between the aluminium terminals under water, which would be sufficient to produce a small percentage of ozone in the oxygen whose absorption was being tested.

The apparatus for the experiment described in Section II was again set up, but in this case a glycerine screen, 1 cm. in thickness, was placed in the path of the light from the Henri spark between the lens and the brass absorption tube. This glycerine screen was found to cut off all radiation below the wave-length $\lambda = 2300 \text{ \AA.U.}$ so that there was no possibility of any radiation entering the oxygen absorption tube which would transform ozone into oxygen. The tube was filled with oxygen at 140 atmospheres pressure and a photograph of the absorption spectrum taken, a reproduction of which is shown in Fig. 4(a). The screen was then removed and the experiment repeated, and the absorption bands shown in Fig. 4(b) were obtained. From these photographs it will be seen that the ultraviolet bands were present in both cases, but when the glycerine screen was inserted the intensity of the light was somewhat reduced so that the bands were shown to better advantage than with the screen removed. However, this experiment showed that these absorption bands were not due to the presence of ozone which may have been formed by ultraviolet light falling on the oxygen gas in the absorption tube.

(c) To make a more definite test as to whether the ultraviolet bands were due to ozone or not, the absorption spectrum of a mixture consisting of a small percentage of ozone in oxygen was obtained in the following way.

The absorption tube in this case consisted of a glass tube 25 cms. long and 1 cm. in diameter with a small side tube sealed in near each end. The ends of the tube were closed by plane parallel plates of clear quartz securely waxed on so that when mounted in position the radiation from the source, which as before, was the Henri spark, passed along the absorption tube through the quartz windows into the slit of the spectrograph. The absorbing gas was obtained by slowly passing oxygen gas through a Heumann ozonizer and the resulting mixture of ozone and oxygen was led in at one end of the absorption tube through the side tube, passing out through the second side tube at the other end. The gas coming from the tube was allowed to escape into the atmosphere, so that the pressure of the

absorbing gas in the tube was approximately one atmosphere. The flow of gas through the ozonizer was started some time before an exposure was made, so as to permit the oncoming gas to sweep out the air from the absorption tube. The percentage of ozone in the mixture in all cases was very small, probably much less than the 1 per cent. mixture used by Professors Fowler and Strutt. The absorption spectrum, when photographed, showed a number of faint symmetrical bands about 7 Å.U. in width in the region extending from the wave-length $\lambda = 2704$ Å.U. to the wave-length $\lambda = 2455$ Å.U. while below this region there was only partial absorption due to the small percentage of ozone used. A comparison spectrum of the absorption due to oxygen at 140 atmospheres was taken and it was found that the bands did not correspond. This is quite evident from Plate I, Fig. 5, which in reproduction (a) gives the oxygen absorption bands, while (b) shows the ozone bands, with the mercury arc shown in (c) as a wave-length standard. The wave-lengths of the ozone bands were measured and the results are given in Table V, from which it will be seen that they do not correspond to the ultraviolet absorption bands found either with liquid or gaseous oxygen. These experiments conclusively showed that the ultraviolet bands obtained in the absorption spectrum of liquid and gaseous oxygen must have been due to oxygen itself, and not to the nitrogen impurity or small percentage of ozone present.

TABLE V

Absorption by Ozone.
Means of Bands

Å.U.	Å.U.	Å.U.	Å.U.
2701	2623	2556	2491
2678	2605	2539	2478
2658	2587	2523	2458
2640	2571	2504	

V. SUMMARY

- (1) The absorption spectrum of oxygen, both liquid and gaseous, between the wave-lengths $\lambda = 7000$ A.U. and $\lambda = 2150$ A.U. has been examined.
- (2) In the visible region eight absorption bands were noted in the case of liquid oxygen and seven with gaseous oxygen.

(3) In the ultraviolet part of the spectrum four broad bands were found both with liquid and also gaseous oxygen, each made up of a set of finer triplet bands. The wave-lengths of these bands were measured and those in the gaseous spectrum were found to be slightly shifted towards the ultraviolet.

(4) Some experiments were performed on the absorption spectra of nitrogen and ozone which were the two most likely impurities present in the oxygen. From the results obtained it was concluded that the bands observed in the absorption spectrum of both liquid and gaseous oxygen were due to oxygen and not to the presence of the impurities mentioned above.

This work was carried out under the direction of Prof. J. C. McLennan to whom the writer wishes to express his most sincere thanks for his advice and many practical suggestions.

The Physical Laboratory,
University of Toronto,
May 15th, 1921.

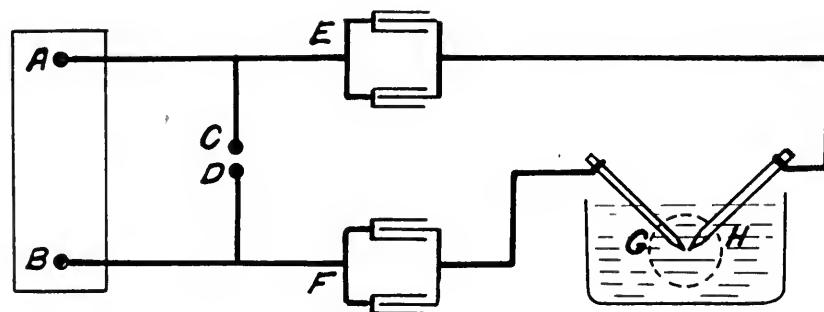


Fig. 1.

Fig. 2.

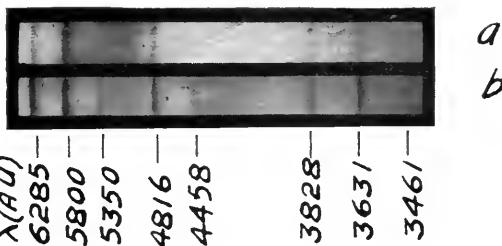


Fig. 3.

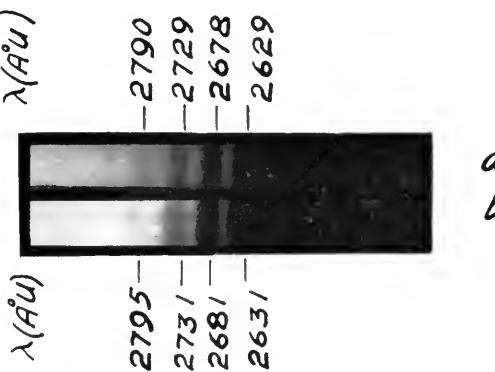


Fig. 4.



Fig. 5.



Plate 1.









On the Permeability of Thin Fabrics and Films to Hydrogen and Helium. By Prof. J. C. McLENNAN, F.R.S., and W. W. SHAVER, B.A., University of Toronto.

I. Introduction.

IN a recent paper by R. T. Elworthy* and V. F. Murray the diffusion of hydrogen and helium through thin rubber fabrics was discussed, and the results of measurements made by them on several samples of balloon fabrics were given. In these experiments the amount of gas diffusing through the fabrics was measured by a Shakespear Katharometer and by a Jamin Interferometer. As the method was one capable of wide application it was decided to use it in determining the permeability of liquid films to various gases, and the following paper describes some experiments made upon the passage of hydrogen and helium through soap films. The study of gas transfusion through membranous tissues is an important physiological problem, and it was thought on this account that it would be useful and might prove interesting to measure the rate of gas diffusion through films of various materials, with a view to formulating a more exact theory of the process of gas transfusion than exists at present.

* Proc. Roy. Soc. Can., May 1919.

II. Preliminary Experiments.

In order to test the apparatus and to acquire a working familiarity with the instruments, a preliminary study of the diffusion of hydrogen through the fabrics used by Elworthy and Murray was made. The apparatus used and the method of assembling it was the same as described in their paper. The fabrics used by them were inserted as a separating diaphragm in an air-tight drum-like vessel. Two gases were brought into this drum, one on either side of the fabric, and their transfusion was determined by tests on the gases by means of the instruments mentioned above. For a full description of the Shakespear apparatus the reader is referred to the paper by Elworthy and Murray. It will suffice here to say that this apparatus was made by the Cambridge Scientific Instrument Co., and that its principle is based on the variation in resistance of a heated platinum coil, constituting one branch of a Wheatstone Bridge circuit, when the gas mixture surrounding the cell has its thermal conductivity varied by changes in its component parts. The two methods adopted were (1) to pass a continuous stream of pure air and one of pure hydrogen on opposite sides of the fabric as a dividing diaphragm, and (2) to enclose a known quantity of pure air on one side and to pass a continuous stream of pure hydrogen past the other side of the fabric.

In the present experiments both methods were followed, but gas tests were made with the katharometer only. It was found that 20°C . was a more suitable temperature for working at than $15^{\circ}5\text{ C}$. as previously used by Elworthy and Murray. The measurements obtained were made by keeping the permeameter and connexions in a thermostat at $20^{\circ}0\text{ C}$., the variation in temperature being not more than $0^{\circ}2\text{ C}$.

III. Calibration.

The katharometer used to detect small percentages of hydrogen or of helium in air had already been calibrated for both gases ; but this calibration was checked by noting the galvanometer deflexions for a given sample of gas, deducing the percentage of helium or hydrogen present from the calibration curve and then checking the result by actually weighing a known volume of the sample studied. It was found that the values obtained by the latter method fitted in very closely with the calibration curve of Elworthy and Murray. It may be stated here that in their work it had

been well established that the curve obtained by plotting galvanometer deflexions against percentages of hydrogen or helium present in air was a straight line through the origin. The calibration showed that (1) 259 mm. deflexion on the scale 1 metre from the galvanometer represented 1 per cent. hydrogen in air, and (2) 163 mm. deflexion on the scale 1 metre from the galvanometer represented 1 per cent. of helium in air.

The following table gives a comparison of the results obtained in the present experiments with those obtained by Elworthy and Murray when using the same fabrics. In each case the permeability is given as being the number of litres of gas permeating 1 square metre of a fabric in 24 hours :—

TABLE I.

Fabric No.	Results obtained in this investigation. Temp. 20° C.		Results obtained by Elworthy and Murray. Temp. 15°5 C.	
	Method I. Using Katharometer.	Method II. Using Katharometer.	Method I. Using Interferometer.	Method II. Using Katharometer.
*II. B	9·6	9·8	8·4	9·5
III. A ...	8·4	8·0	0	8·6
IV.	5·0	...	5·5	4·7
V. B	6·3	...	6·7	6·4
VI. A ...	8·0	8·1
VI. C.....	7·8	7·5	...	8·1
XII.	5·4

IV. Permeability of Films.

After the preliminary experiments had been made, an attempt was made to employ the same method in making a determination of the transfusion of hydrogen and of helium through a soap film. Sir James Dewar † in a paper presented at a meeting of the Royal Institution of Great Britain in Jan. 1917, described many interesting experiments with long-lived soap bubbles and films, among them being a determination of what he calls "gas transference" through

* The fabric numbers refer to samples of balloon fabrics described in the papers by Elworthy and Murray.

† Dewar, Paper, "Soap Bubbles of Long Duration," presented at weekly meeting of the Royal Institution of Great Britain, Jan. 19, 1917.

a soap bubble, by blowing a hydrogen bubble in hydrogen and noting the decrease in diameter as time went on, due to the slight excess pressure inside the bubble. What he measured was the excess of the rate of gas diffusion outward over the rate inward through the film, and he found that as the soap bubble became thinner the gas transference became greater. In the present experiment the endeavour was to determine the actual rate of gas flow per square centimetre through the film, keeping the film as nearly constant in composition and thickness as possible.

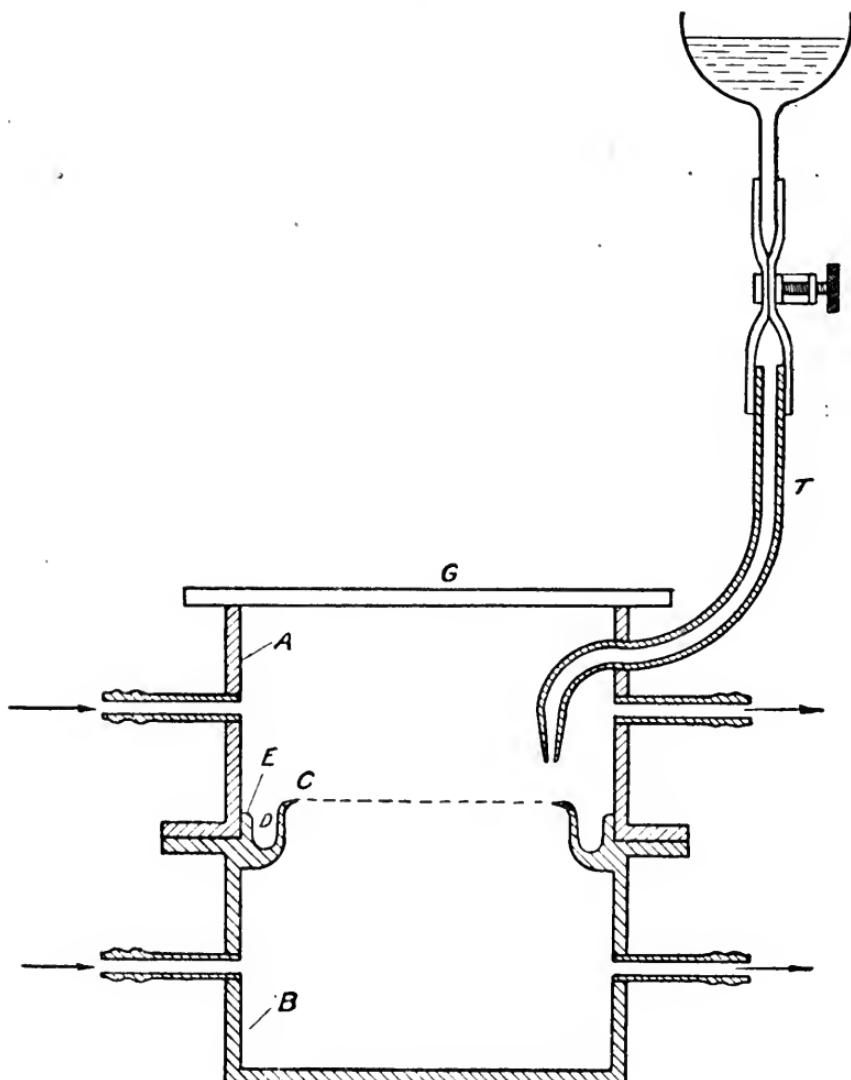
V. Description of Apparatus.

A small cylindrical brass chamber (see fig. 1) was made for the film in two sections with a ground brass joint, which, when covered with soft wax and pressed together, made the vessel air-tight. Each section was 4·1 cm. in diameter and 7·0 cm. in height, having inlet and outlet tubes as shown in the diagram. The top section A, fig. 1, was closed by a window of plate glass, G, put on with hard wax, so that when a source of light was held directly over the chamber, its image in the film could be distinctly seen and in this way the character of the surface of the film—whether concave, convex, or plane—was known at once by the character of the image produced. Knowing the curvature of the film one could adjust the pressures of hydrogen and air on either side very accurately and so as to keep the film plane and therefore eliminate the diffusion due to excess pressure on either side. The brass ring C, fig. 1, supporting the film was 4·95 cm. in diameter, and ground down to a sharp edge. An annular channel, D, was made in the outer part of the supporting ring, and the whole soldered in the lower section of the film chamber, leaving about 0·6 cm. of the brass ring projecting above the wax surface. In this way the soft wax used in making the joint air-tight was prevented from contaminating the film and destroying its surface tension.

To overcome the difficulty of evaporation and drainage from the film, that is to keep its composition and thickness constant, the air and hydrogen used were both saturated with water vapour before entering the chamber, and, in addition, a means of adding solution to the film was provided in the following way. A bent tube, T, was inserted in the upper chamber as indicated in the diagram, having a thistle tube connected to the outer end by rubber tubing. A small amount of the same soap solution used in making the film was poured into the thistle tube and a drop of this was

allowed to fall on the film at short intervals (say, every two or three minutes), the flow being regulated by a clamp on the rubber tubing. The excess solution drained off the edges

Fig. 1.



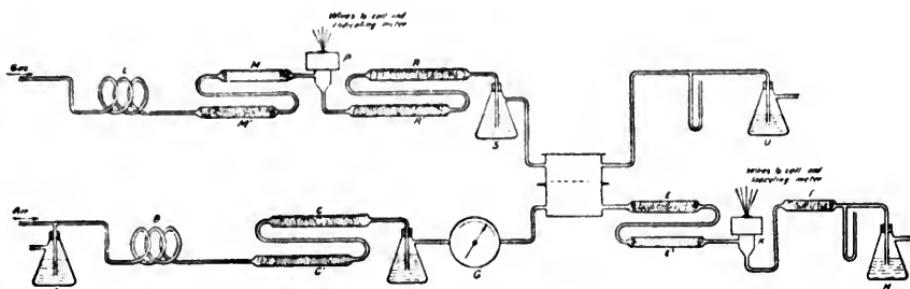
of the film into the lower section of the chamber. In this way the film was kept at a practically constant maximum thickness and the variations in diffusion due to changes in the film were eliminated as far as possible.

The air was let in through a T-tube A (see fig. 2), which permitted the rate of flow to be varied by raising or lowering the water level. With any given level the pressure was adjusted so that the air always gently bubbled through the base of the T-tube. In its course through the system the air passed through a copper warming coil B and two tubes filled with cotton wool moistened with glycerine so as to eliminate all dust particles, as it was found that the introduction of dust particles soon caused the soap films to rupture. It was then bubbled through water and led through a gas-meter which measured the rate of flow. From the gas-meter the air, saturated with water vapour, was led through the lower section of the film chamber, D, sweeping out with it the hydrogen gas which diffused through the film. From there the air was dried in the phosphorus pentoxide tubes E and E', and tested by the katharometer K, finally bubbling out through the water in H at a pressure of about 1 cm. of water.

VII. Gas Circuit.

The gas circuit shown in fig. 2 was somewhat similar, except that the gas was tested before entering the film chamber by a purity meter P, of the katharometer type,

Fig. 2.



and then passed through the cotton wool tubes R and R', bubbled through water in the bottle S, and thence to the film chamber, and, finally, bubbled out through water in U, at a pressure of about 1 cm. of water. The pressure of the gas in the circuit was altered very slightly by adjusting the tube U, so that the film surface remained plane. The rate of flow used was about 2 litres per hour.

VIII. General Procedure. -

When readings were taken the air and the gas under test were allowed to flow past the film until the katharometer reading giving the percentage of gas in the air was steady. This required one half hour, and then readings were taken at two minute intervals for forty minutes, and note was taken of the rate of flow of air by means of the gas meter. This ranged from 2 to 10 litres per hour. After one set of readings was taken, if the film still remained intact, the rate of air flow was changed, and after conditions became steady again another set of results was obtained. In this way as many as four sets of readings were taken without renewing the film.

IX. Purity of Gases.

The purity of the gases under test was in both cases comparatively high. The hydrogen was obtained from a commercial supply which was guaranteed to be of 99 per cent. purity. The helium used was first purified by passing it through a set of four charcoal tubes at the temperature of liquid air. Its purity was tested by means of a quartz density balance, and found to be 99·2 per cent.

X. Soap Solution.

The soap solution used was one made up according to Boys' formula, and contained 2 per cent. sodium oleate, 24 per cent. glycerine, and 74 per cent. water, with a few drops of strong ammonia.

XI. Results.

The following are the results obtained. The last column gives the number of cubic centimetres of gas transfusing through one square centimetre of film per hour.

The readings were taken at room temperature which varied slightly as shown in the table. However, taking the average values obtained for the two gases, we find the ratio of the transfusion of helium to that of hydrogen to be 0·70. In the case of balloon fabrics, Elworthy and Murray found this ratio to be 0·67. Expressing the average results for hydrogen and helium in the case of a soap film in the same terms as the permeability of balloon fabrics, we find the permeability of films to these gases given by Elworthy and Murray for

TABLE II.

(a) *Hydrogen.*

Duration of film. H. min.	Temp. °C.	Transfusion of gas in c.c. per sq. cm. of film per hour.
1 52	18·6	4·8
1 35	20·0	5·2
0 59	20·1	4·2
1 45	19·6	4·3
1 20	20·8	3·5
1 10	19·7	4·1
1 07	19·1	3·8
4 40	19·2	3·1
	19·1	3·1
	19·2	3·8
	19·1	3·6
Average ...		4·0

(b) *Helium.*

3 41	18·4	3·0
	18·3	2·4
	18·0	3·1
5 15	19·5	2·2
	19·3	2·8
	18·7	2·8
	18·7	3·1
Average		2·8

hydrogen to be 960 and for helium 670 litres per square metre per day. For the most highly porous balloon fabrics tested by Elworthy and Murray the transfusion of hydrogen was only about 10·0 litres per square metre per day, and of helium 7·1 litres per square metre per day. It is interesting to note that while soap films were very much more permeable to hydrogen and helium than were the balloon fabrics tested, the ratios of the permeabilities of both fabrics and films to the two gases were practically the same. This is the more interesting when it is considered that while in the case of the films the membrane was of the continuous type, in the case of the fabric there was a possibility of the diaphragm being discontinuous. It may be, however, that on account of the fabrics being "doped" the discontinuity referred to was negligible. In this case the process of transfusion of the gases through the substance of the fabric would probably be of the same nature as that of transfusion through the films.

XII. Diffusion of Hydrogen through Wet and Dry Cotton Fabrics.

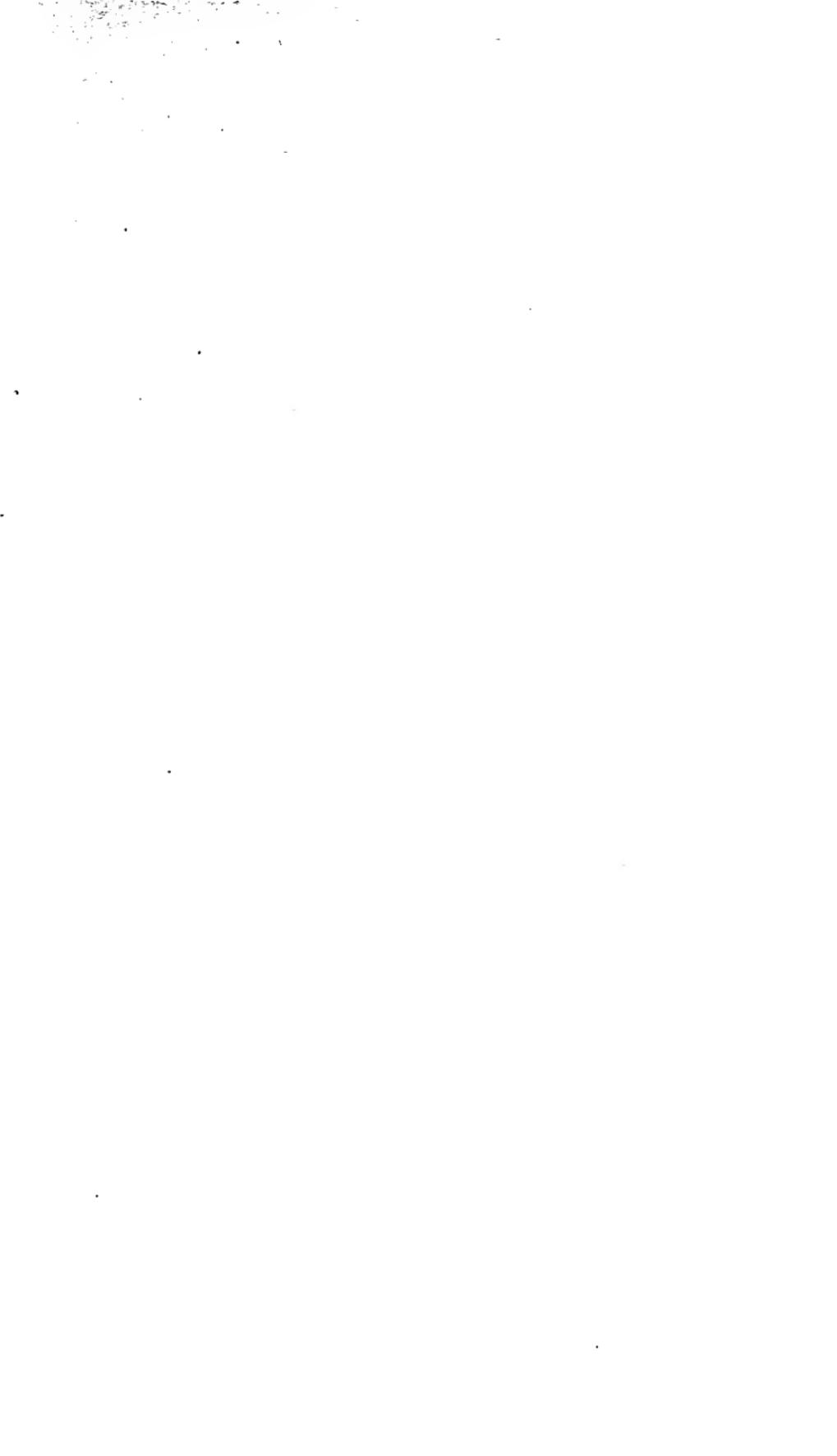
Some experiments were made on the transfusion of hydrogen through a closely woven cotton fabric when wet and also when dry. When this fabric was dry the gas diffused through it so rapidly that it was impossible to obtain a measure of the rate of transfusion with the katharometer. On the other hand, when the fabric was thoroughly wetted with distilled water it was found that the transfusion of hydrogen through it was so slow that it could not be detected with the katharometer, even when the rate of flow of the air past the fabric was reduced to as low a value as 2·4 litres per hour.

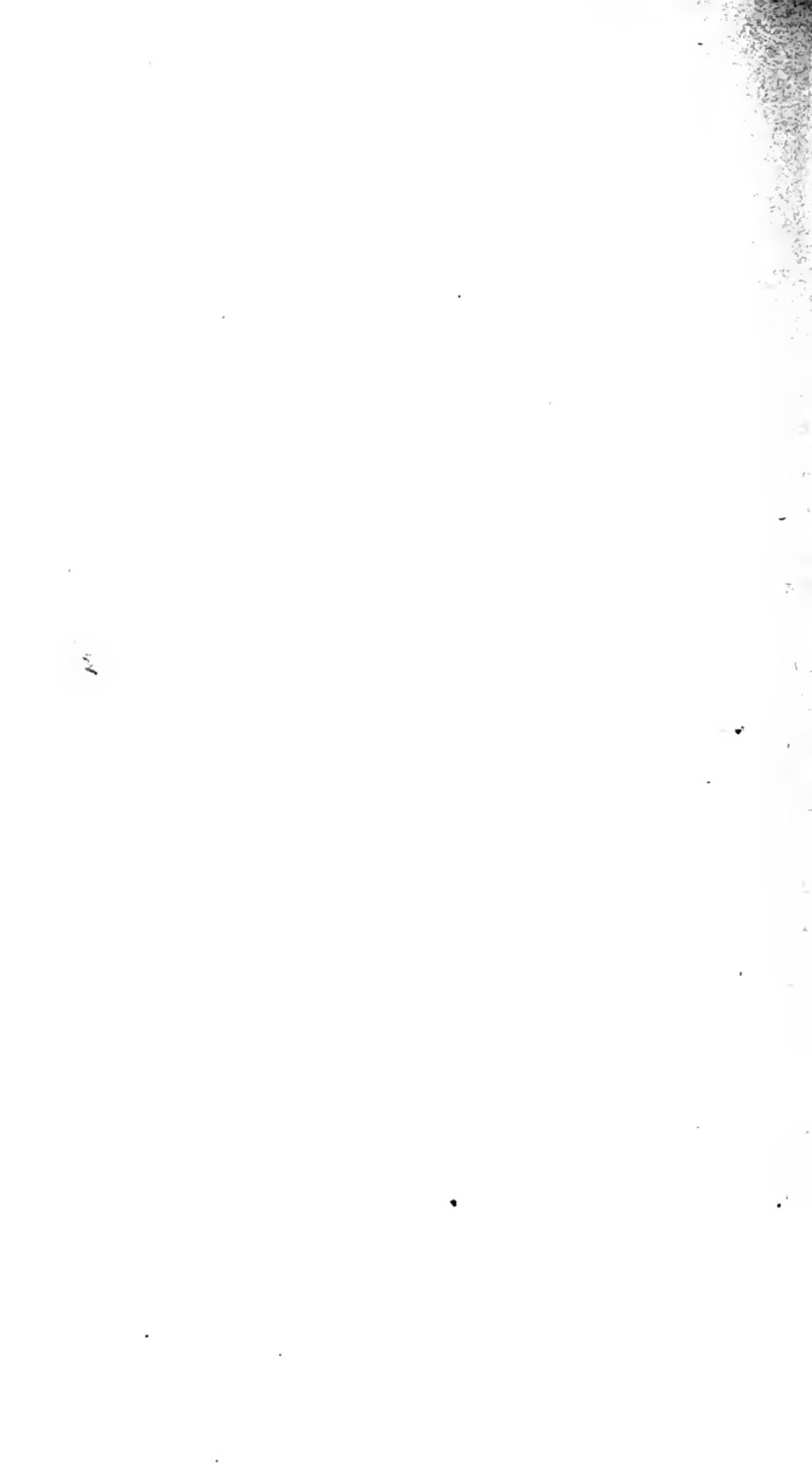
It was noted in the experiments on the transfusion of hydrogen through soap films that as soon as the film became thinner than the red-green stage the rate of diffusion rapidly increased. It is evident, therefore, that the rate of diffusion depends very largely on the thickness of the films used. In the case of the wet cotton fabrics the thickness of the water films filling up the interstices was very much greater than that of the soap films investigated.

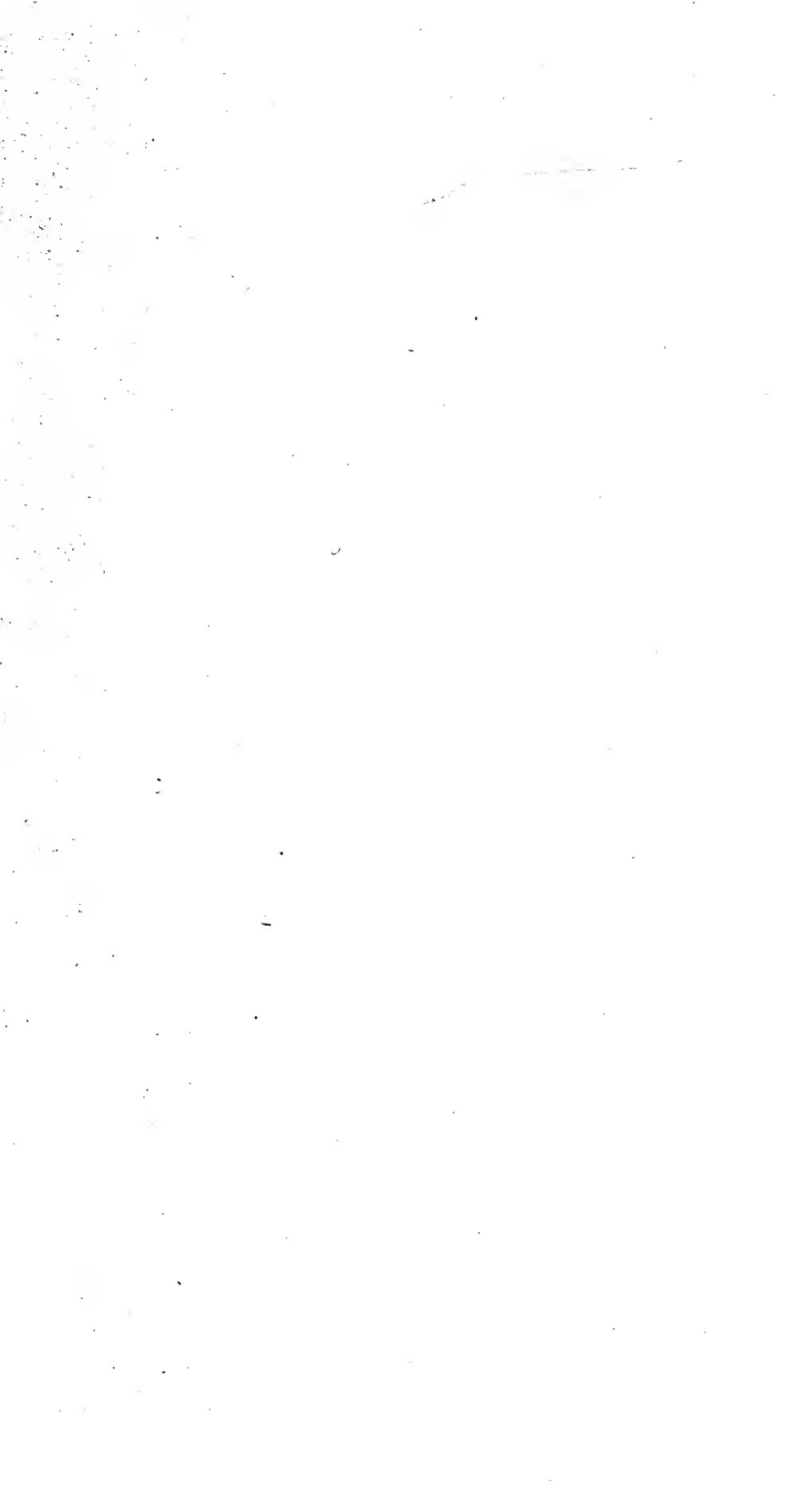
XIII. Summary of Results.

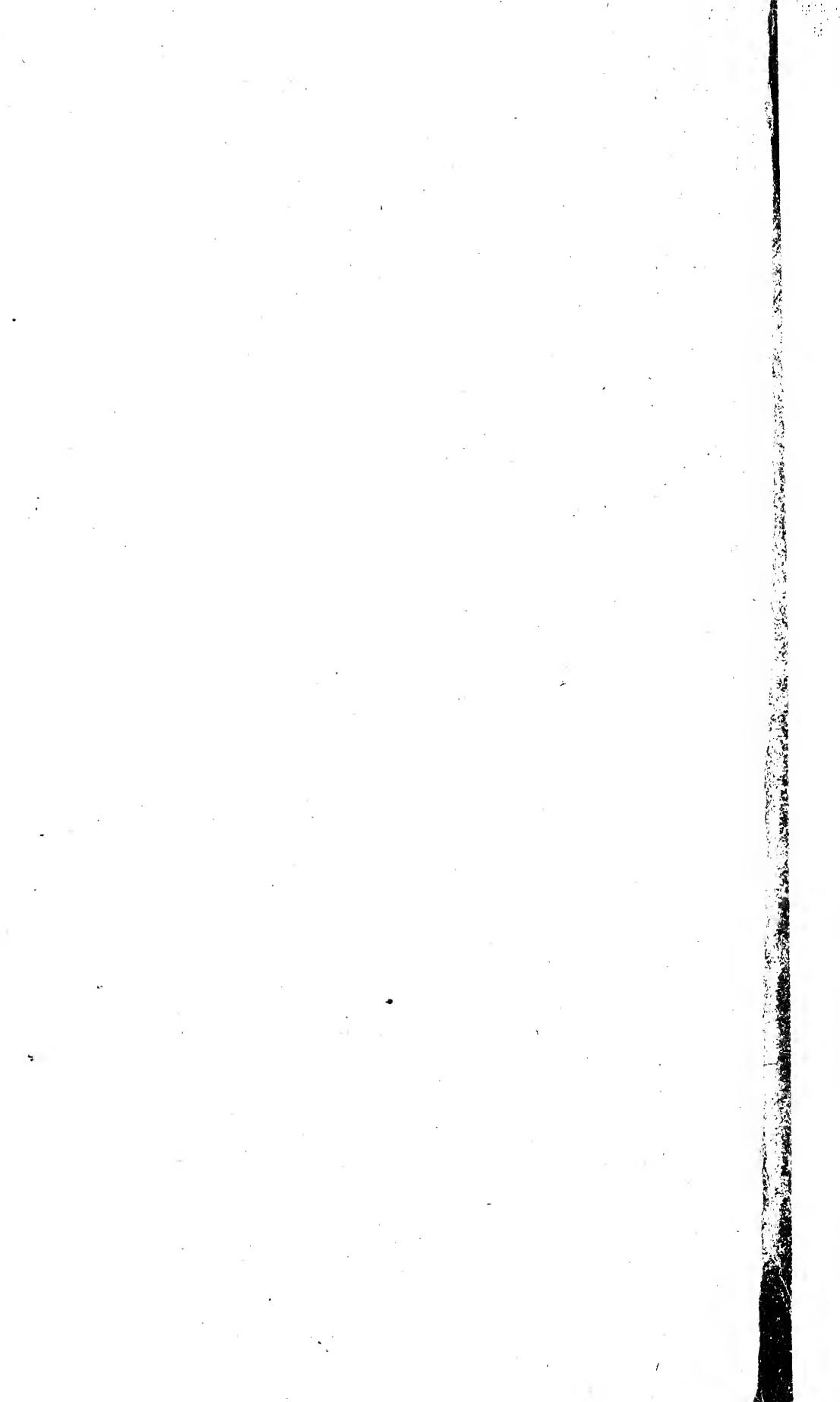
1. The rate of diffusion of hydrogen through a series of balloon fabrics has been determined.
2. The permeability of soap films whose thickness corresponds to the red-green stage has been found for helium to be 670 litres per square metre per day and for hydrogen 960 litres per square metre per day at 20° C.
3. The rate of transfusion of helium through soap films has been shown to be 0·70 of that of hydrogen through similar films.
4. The diffusion of hydrogen through water films filling the interstices of a wet cotton fabric has been shown to be very low; with soap films showing interference colours the rate of diffusion of both hydrogen and helium was found to be considerable.

The Physical Laboratory,
University of Toronto.
May 15th, 1920.









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